

6. POTENTIAL FOR HUMAN EXPOSURE

6.1 OVERVIEW

Nickel has been identified in at least 862 of the 1,636 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2003). However, the number of sites evaluated for nickel is not known. The frequency of these sites can be seen in Figure 6-1. Of these sites, 855 are located within the United States, 5 are located in the Commonwealth of Puerto Rico, and 2 are located in the Territory of Guam (the Commonwealth of Puerto Rico and the Territory of Guam are not shown).

Nickel and its compounds are naturally present in the earth's crust, and releases to the atmosphere occur from natural discharges such as windblown dust and volcanic eruptions, as well as from anthropogenic activities. It is estimated that 8.5 million kg of nickel are emitted into the atmosphere from natural sources such as windblown dust, volcanoes, and vegetation each year. Five times that quantity is estimated to come from anthropogenic sources. The burning of residual and fuel oil is responsible for 62% of anthropogenic emissions, followed by nickel metal refining, municipal incineration, steel production, other nickel alloy production, and coal combustion (Bennett 1984; Schmidt and Andren 1980). Table 6-1 lists releases from facilities in the United States that produced, processed, or used nickel in 2001, according to TRI (TRI01 2003). These releases, which totaled 2,904,982 pounds (1,318,862 kg), were distributed as follows: 85.4% to land, 11.0% to air, 0.7% to water, and 0.8% to underground injection. Table 6-2 lists releases from facilities in the United States that produced, processed, or used nickel compounds in 2001, according to TRI (TRI01 2003). These releases, which totaled 53,214,334 pounds (24,159,307 kg), were distributed as follows: 95.8% to land, 1.9% to air, 0.5% to water, and 1.8% to underground injection. The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

The general population is exposed to low levels of nickel in ambient air, water, and food. Exposure also occurs from smoking. The general population takes in most nickel through food. The average daily dietary nickel intake for U.S. diets is 69–162 μg (O'Rourke et al. 1999; Pennington and Jones 1987; Thomas et al. 1999). These values agree with those from European studies. Typical average daily intakes of nickel from drinking water and air are approximately 8 and 0.04 μg , respectively. The highest general population exposures to nickel are typically observed in nickel refineries. This is reflected, for example,

5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

Figure 6-1. Frequency of NPL Sites with Nickel Contamination

6. POTENTIAL FOR HUMAN EXPOSURE

Table 6-1. Releases to the Environment from Facilities that Produce, Process, or Use Nickel

Reported amounts released in pounds per year ^a								
State ^b	Number of facilities	Air ^c	Water	Under-ground injection	Land	Total on-site release ^d	Total off-site release ^e	Total on and off-site release
AL	51	4,267	815	0	292	5,374	64,086	69,460
AR	34	15,870	20	0	2,920	18,810	16,512	35,322
AZ	21	1,052	No data	0	621,654	622,706	5,340	628,046
CA	103	2,538	579	0	661,818	664,935	32,720	697,655
CO	14	564	5	0	10,255	10,824	8,209	19,033
CT	51	2,641	1,037	0	0	3,678	198,750	202,428
DE	1	0	No data	0	0	0	250	250
FL	22	1,293	58	3,375	0	4,726	32,333	37,059
GA	39	5,262	408	0	142	5,812	10,782	16,594
IA	54	3,083	1,036	0	399	4,518	42,706	47,224
ID	3	65	No data	0	232,200	232,265	No data	232,265
IL	131	11,559	2,448	0	174,167	188,174	142,179	330,353
IN	142	38,719	517	0	5,676	44,912	3,765,019	3,809,931
KS	21	2,051	0	0	10	2,061	2,382	4,443
KY	54	103,156	95	4,766	38,290	146,307	56,547	202,854
LA	24	966	614	0	16,803	18,383	38,609	56,992
MA	46	4,285	428	0	416	5,129	81,259	86,388
MD	13	2,300	No data	0	0	2,300	1,949	4,249
ME	12	336	305	0	0	641	7,236	7,877
MI	117	17,594	1,337	0	4,395	23,326	244,455	267,781
MN	43	1,303	5	0	0	1,308	108,685	109,993
MO	50	5,418	275	0	39,049	44,742	47,671	92,413

6. POTENTIAL FOR HUMAN EXPOSURE

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Reported amounts released in pounds per year ^a								
State ^b	Number of facilities	Air ^c	Water	Under-ground injection	Land	Total on-site release ^d	Total off-site release ^e	Total on and off-site release
MS	23	2,439	20	0	910	3,369	1,888	5,257
MT	1	60	No data	0	238,000	238,060	No data	238,060
NC	61	10,827	334	0	260	11,421	181,954	193,375
ND	6	35	3	0	3	41	2,427	2,468
NE	20	2,199	93	0	5	2,297	15,250	17,547
NH	15	945	9	0	0	954	28,642	29,596
NJ	21	5,908	1	0	0	5,909	13,009	18,918
NM	5	892	1	0	255	1,148	313	1,461
NV	5	6,432	0	0	250	6,682	1,000	7,682
NY	67	34,043	384	0	7,798	42,225	76,020	118,245
OH	217	30,038	2,662	0	49,305	82,005	617,283	699,288
OK	67	5,191	204	0	108,736	114,131	28,430	142,561
OR	19	3,654	150	0	30,389	34,193	41,940	76,133
PA	218	24,168	1,297	0	7,016	32,481	546,197	578,678
PR	3	0	No data	0	250	250	0	250
RI	8	511	5	0	0	516	5,733	6,249
SC	43	2,511	387	0	9,321	12,219	261,771	273,990
SD	6	262	No data	0	0	262	338	600
TN	52	4,321	267	0	66,508	71,096	66,463	137,559
TX	130	7,022	3,401	14,523	81,007	105,953	368,361	474,314
UT	18	623	0	0	8,600	9,223	3,342	12,565
VA	21	1,742	383	0	5	2,130	8,945	11,075
VT	6	0	No data	0	0	0	608	608

6. POTENTIAL FOR HUMAN EXPOSURE

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State ^b	Number of facilities	Air ^c	Water	Under-ground injection	Land	Total on-site release ^d	Total off-site release ^e	Total on and off-site release
WA	17	1,766	809	0	6,987	9,562	45,213	54,775
WI	146	10,807	565	0	16,264	27,636	147,976	175,612
WV	14	332	5	5	21,308	21,650	1,512	23,162
WY	3	48	0	0	18,590	18,638	10	18,648
Total	2258	381,098	20,962	22,669	2,480,253	2,904,982	7,372,304	10,277,286

Source: TRI01 2003

^aData in TRI are maximum amounts released by each facility.^bPost office state abbreviations are used.^cThe sum of fugitive and stack releases are included in releases to air by a given facility.^dThe sum of all releases of the chemical to air, land, water, and underground injection wells.^eTotal amount of chemical transferred off-site, including to publicly owned treatment works (POTW).

6. POTENTIAL FOR HUMAN EXPOSURE

Table 6-2. Releases to the Environment from Facilities that Produce, Process, or Use Nickel Compounds

Reported amounts released in pounds per year ^a								
State ^b	Number of facilities	Air ^c	Water	Under-ground injection	Land	Total on-site release ^d	Total off-site release ^e	Total on and off-site release
AK	5	63	147	43,000	1,229,689	1,272,899	262	1,273,161
AL	30	8,937	7,182	0	895,880	911,999	134,786	1,046,785
AR	15	12,780	1,014	0	946,777	960,571	71,175	1,031,746
AZ	13	6,610	0	0	750,699	757,309	13,968	771,277
CA	70	5,062	1,485	0	845,882	852,429	203,254	1,055,683
CO	9	1,450	6	0	29,179	30,635	20,236	50,871
CT	24	1,803	3,879	0	0	5,682	291,645	297,327
DC	1	0	No data	0	0	0	11	11
DE	7	33,951	1,975	0	70,147	106,073	73,990	180,063
FL	26	175,369	4,204	0	631,991	811,564	208,053	1,019,617
GA	25	8,657	10,221	0	537,378	556,256	18,571	574,827
HI	1	42,500	5	0	0	42,505	250	42,755
IA	17	92,848	32,851	0	124,030	249,729	158,889	408,618
ID	3	1,421	5	0	56,557	57,983	0	57,983
IL	94	28,661	1,556	0	538,247	568,464	504,405	1,072,869
IN	78	31,156	8,139	250	1,453,416	1,492,961	630,254	2,123,215
KS	13	2,567	0	0	70,315	72,882	20,295	93,177
KY	41	18,395	32,400	0	982,983	1,033,778	155,386	1,189,164
LA	33	8,644	6,923	2,850	194,728	213,145	456,795	669,940
MA	19	20,322	585	0	23,531	44,438	163,504	207,942
MD	12	45,799	3,139	533	24,452	73,923	110,054	183,977
ME	3	935	470	0	0	1,405	7,205	8,610

6. POTENTIAL FOR HUMAN EXPOSURE

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MI	72	26,240	1,553	0	4,133,770	4,161,563	2,238,774	6,400,337
MN	22	14,202	330	0	79,480	94,012	187,510	281,522
MO	33	10,367	4,922	0	576,710	591,999	123,946	715,945
MS	15	24,966	1,342	62,000	93,266	181,574	274,472	456,046
MT	7	1,382	1	227,070	432,045	660,498	106,064	766,562
NC	29	7,143	2,248	0	517,317	526,708	3,263	529,971
ND	4	4,174	11	0	72,800	76,985	50,683	127,668
NE	9	453	30	0	95,515	95,998	3,981	99,979
NH	5	344	5	0	860	1,209	8,903	10,112
NJ	17	4,401	8,542	0	14,283	27,226	54,906	82,132
NM	5	452	1	0	435,293	435,746	0	435,746
NV	11	2,744	687	6	24,369,117	24,372,554	1,247	24,373,801
NY	28	9,796	38,067	0	99,968	147,831	271,609	419,440
OH	96	19,524	9,013	606,600	861,928	1,497,065	2,790,023	4,287,088
OK	16	7,677	719	0	73,310	81,706	48,301	130,007
OR	11	2,392	250	0	51,263	53,905	2,181	56,086
PA	114	99,552	11,377	0	465,609	576,538	2,773,485	3,350,023
PR	8	87,442	971	0	0	88,413	60,338	148,751
RI	6	253	261	0	250	764	3,719	4,483
SC	37	3,314	2,581	0	164,531	170,426	94,780	265,206
SD	1	216	No data	0	20,000	20,216	0	20,216
TN	38	3,618	10,581	0	512,229	526,428	204,563	730,991
TX	96	18,977	6,515	38,380	498,227	562,099	740,460	1,302,559

6. POTENTIAL FOR HUMAN EXPOSURE

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State ^b	Number of facilities	Air ^c	Water	Under-ground injection	Land	Total on-site release ^d	Total off-site release ^e	Total on and off-site release
UT	10	2,117	6,300	0	6,969,075	6,977,492	881	6,978,373
VA	23	55,238	3,095	0	311,312	369,645	67,020	436,665
VI	1	196	0	0	1,773	1,969	4,925	6,894
WA	7	1,117	840	0	75,227	77,184	1,933	79,117
WI	44	3,941	2,385	0	2,804	9,130	126,143	135,273
WV	17	41,463	16,033	0	518,525	576,021	266,001	842,021
WY	3	3,063	0	0	131,737	134,800	0	134,800
Total	1324	1,004,693	244,846	980,689	50,984,105	53,214,334	13,753,100	66,967,434

Source: TRI01 2003

^aData in TRI are maximum amounts released by each facility.^bPost office state abbreviations are used.^cThe sum of fugitive and stack releases are included in releases to air by a given facility.^dThe sum of all releases of the chemical to air, land, water, and underground injection wells.^eTotal amount of chemical transferred off-site, including to publicly owned treatment works (POTW).

6. POTENTIAL FOR HUMAN EXPOSURE

in the intakes of nickel from water and air reported in Sudbury, Ontario, Canada, of 140 and 15 $\mu\text{g}/\text{day}$, respectively. However, this source of exposure to nickel is not a concern for U.S. populations, due to the absence of refinery operations in the United States. Other potential sources of nickel exposure are from contaminated intravenous fluids, dialysis, and leaching and corrosion of nickel from prostheses.

Occupational exposure to nickel may occur by dermal contact or by inhalation of aerosols, dusts, fumes, or mists containing nickel. Dermal contact may also occur with nickel solutions, such as those used in electroplating, nickel salts, and nickel metal or alloys. Nickel-containing dust may be ingested where poor work practices exist or where poor personal hygiene is practiced. A National Occupational Exposure Survey (NOES) conducted by NIOSH from 1981 to 1983 estimates that 727,240 workers are potentially exposed to some form of nickel metal, alloys, salts, or inorganic nickel compounds in the United States (NIOSH 1990). The forms of nickel that these workers were probably exposed to and the levels of exposure for different industries and operations were reviewed by Warner (1984) and IARC (1990).

Information on nickel exposure from hazardous waste sites is lacking. The most probable route of exposure from hazardous waste sites would be from consumption of contaminated drinking water, inhalation of dust, dermal contact with bath/shower water, soil, or dust, and ingestion of nickel-contaminated soil. Groundwater contamination may occur where the soil has a coarse texture and where acid waste, such as waste from plating industries, is discarded. However, there is no information linking this source of nickel contamination in groundwater to levels of nickel in drinking water that would be of concern ($>50 \mu\text{g}/\text{L}$).

Nickel releases to the atmosphere are mainly in the form of aerosols that cover a broad spectrum of sizes. Particulates from power plants tend to be smaller than those from smelters (Cahill 1989; Schroeder et al. 1987). Atmospheric aerosols are removed by gravitational settling and dry and wet deposition. Submicron particles may have atmospheric half-lives as long as 30 days (Schroeder et al. 1987). Monitoring data confirm that nickel can be transported far from its source (Pacyna and Ottar 1985). Average ambient air nickel concentrations in the United States measured during 1977–1982 ranged between 7 and 12 ng/m^3 (EPA 1986a). A recent estimate of ambient nickel concentrations in the United States based on data collected in 1996 is 2.22 ng/m^3 (EPA 2003u). Nickel concentrations in air particulate matter in remote, rural, and U.S. urban areas have been found in the ranges from 0.01–60, 0.6–78, and 1–328 ng/m^3 , respectively (Schroeder et al. 1987). Nickel concentrations in indoor air are typically $<10 \text{ ng}/\text{m}^3$.

6. POTENTIAL FOR HUMAN EXPOSURE

The form of nickel emitted to the atmosphere varies according to the type of source. Nickel species associated with combustion, incineration, and metals smelting and refining are often complex nickel oxides, nickel sulfate, and metallic nickel, and in more specialized industries, the species commonly found are nickel silicate, nickel subsulfide, and nickel chloride (EPA 1985a).

Uncontaminated freshwater and seawater generally contain about 0.300 µg/L of nickel (Barceloux 1999). Concentrations of nickel in drinking water commonly range between 0.55 and 25 µg/L and average between 2 and 4 µg/L. The concentration of nickel in rain has been reported as ≤ 1.5 µg/L (1.5 ppb). Concentrations of nickel in snow in Montreal, Canada, ranged from 2 to 300 ppb (Landsberger et al. 1983).

Nickel is a natural constituent of soil; levels vary widely depending on local geology and anthropogenic input. The typical concentrations of nickel reported in soil range from 4 to 80 ppm. Nickel may be transported into streams and waterways from the natural weathering of soil as well as from anthropogenic discharges and runoff. This nickel accumulates in sediment. Nickel levels in surface water are low. In some studies, nickel could not be detected in a large fraction of analyzed samples. Median nickel concentrations in rivers and lakes range from ≈ 0.5 to 6 µg/L. Levels in groundwater appear to be similar to those in surface water. Levels in seawater are typically 0.1–0.5 µg/L.

The speciation and physicochemical state of nickel is important in considering its behavior in the environment and availability to biota. For example, the nickel incorporated in some mineral lattices may be inert and have no ecological significance. Most analytical methods for nickel do not distinguish the form of nickel; the total amount of nickel is reported, but the nature of the nickel compounds and whether they are adsorbed to other material is not known. This information, which is critical in determining nickel's lability and availability, is site specific. Therefore, it is impossible to predict nickel's environmental behavior on a general basis.

Little is known concerning the chemistry of nickel in the atmosphere. The probable species present in the atmosphere include soil minerals, nickel oxide, and nickel sulfate (Schmidt and Andren 1980). In aerobic waters at environmental pHs, the predominant form of nickel is the hexahydrate $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ ion (Richter and Theis 1980). Complexes with naturally occurring anions, such as OH^- , SO_4^{2-} , and Cl^- , are formed to a small degree. Complexes with hydroxyl radicals are more stable than those with sulfate, which in turn are more stable than those with chloride. $\text{Ni}(\text{OH})_2^0$ becomes the dominant species above pH 9.5. In

6. POTENTIAL FOR HUMAN EXPOSURE

anaerobic systems, nickel sulfide forms if sulfur is present, and this limits the solubility of nickel. In soil, the most important sinks for nickel, other than soil minerals, are amorphous oxides of iron and manganese. The mobility of nickel in soil is site specific depending mainly on soil type and pH. The mobility of nickel in soil is increased at low pH. At one well-studied site, the sulfate concentration and the surface area of soil iron oxides were also key factors affecting nickel adsorption (Richter and Theis 1980).

6.2 RELEASES TO THE ENVIRONMENT

Most analytical methods for nickel in environmental samples do not distinguish between compounds of nickel or the nature of its binding to soil and particulate matter. It is generally impossible to say with certainty what forms of nickel are released from natural and anthropogenic sources, what forms are deposited or occur in environmental samples, and to what forms of nickel people are exposed. The form of nickel has important consequences as far as its transport, transformations, and bioavailability are concerned.

6.2.1 Air

Nickel and its compounds are naturally present in the earth's crust, and releases to the atmosphere occur from natural processes such as windblown dust and volcanic eruption, as well as from anthropogenic activities. These latter releases are mainly in the form of aerosols. It is important to consider the background levels that are due to natural sources and distinguish them from levels that may result from anthropogenic activities. It is estimated that 8.5 million kg of nickel are emitted into the atmosphere from natural sources each year (Bennett 1984; Schmidt and Andren 1980). Based on this value, sources of nickel have been estimated as follows: windblown dust, 56%; volcanoes, 29%; vegetation, 9%; forest fires, 2%; and meteoric dust, 2%. A more recent and higher estimate of 30 million kg/year has been given for emission of nickel into the atmosphere from natural sources (Duce et al. 1991; Giusti et al. 1993). Anthropogenic sources of atmospheric nickel include nickel mining, smelting, refining, production of steel and other nickel-containing alloys, fossil fuel combustion, and waste incineration.

Emissions factors (i.e., kg of nickel emissions per unit consumption or production) have been estimated for various source categories, and these have been used to estimate worldwide emissions (Nriagu and Pacyna 1988). According to Schmidt and Andren (1980), annual anthropogenic emissions are estimated to contain 43 million kg of nickel (median value), 1.4 times the natural emission rate of 30 million

6. POTENTIAL FOR HUMAN EXPOSURE

kg/year. Nriagu and Pacyna (1988) estimate annual anthropogenic emissions as 55.6 million kg. The nickel emission factor for burning residual and fuel oil is estimated to be 0.03 kg/ton, yielding nickel emissions of 26.7 million kg/year or 62% of the total anthropogenic emissions (Schmidt and Andren 1980). The estimated contributions of other anthropogenic sources of nickel are nickel metal and refining, 17%; municipal incineration, 12%; steel production, 3%; other nickel-containing alloy production, 2%; and coal combustion, 2% (Bennett 1984; Schmidt and Andren 1980). Wood combustion is also an important source of nickel emissions (Nriagu and Pacyna 1988).

Table 6-1 lists the air releases from facilities in the United States that produce, process, or use nickel, according to the 2001 TRI (TRI01 2003). These releases, totaling 381,098 pounds (173,018 kg), constitute 11.0% of the environmental releases reported for nickel in the TRI. Table 6-2 lists the air releases from facilities in the United States that produce, process, or use nickel compounds, according to the 2001 TRI (TRI01 2003). These releases, totaling 1,004,693 pounds (456,130 kg), constitute 1.9% of the environmental releases reported for nickel compounds in the TRI. The TRI data listed in Tables 6-1 and 6-2 should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

Based on data contained in EPA's 1996 National Toxics Inventory (NTI) which is compilation of emissions data obtained from TRI, state and local databases, and other studies required by the Clean Air Act (CAA), it is estimated that emissions of nickel compounds into air totaled 1,330 tons per year in the United States (EPA 2000). Of this total, 1,196 tons of nickel compounds per year were derived from urban sources, with the major contributors coming from stationary sources that release 10 or more tons of nickel compounds per year. Onroad mobile sources, such as cars, motorcycles, trucks, and buses, accounted for only 10 tons per year of nickel released to air, whereas nonroad mobile sources, such as airplanes, boats, and lawn mowers, accounted for a release of 66 tons of nickel compounds per year.

Deposition of metals around large smelter complexes is a significant local problem. For example, at the Copper Cliff smelter in Sudbury, Ontario, it is estimated that 42% of nickel particulates emitted from the 381-m stack are deposited within a 60-km radius of the smelter (Taylor and Crowder 1983). The Copper Cliff smelter, one of three large nickel sources in the Sudbury area, emits 592 pounds (269 kg) of nickel per day. In another example, the soils in the 4,000 km² area surrounding the Severonickel Smelter Complex located on the Kola Peninsula, Russia, contain nickel at concentrations that range between 6 and 1,500 times the European background levels of nickel in soils (Barcan 2002). Concentrations of 9,000 mg of nickel per kg of soil (0.9%) have been measured near the smelter. It has been estimated that

6. POTENTIAL FOR HUMAN EXPOSURE

110,000 tons of nickel have been emitted from the smelter into the atmosphere since 1962, with current (2001) emissions of 1,212 tons/year or 3,320 kg/day.

A typical, modern, coal-fired power plant emits ≈ 25 μg nickel per Megajoule (MJ) of power produced, compared with 420 $\mu\text{g}/\text{MJ}$ for an oil-fired plant (Hasanen et al. 1986). The nickel concentration in stack emissions from a modern coal-fired power plant with an electrostatic precipitator was $1.3 \mu\text{g}/\text{m}^3$ (Lee et al. 1975). In a case study of the emissions of metals from an average sized coal-burning electric power plant (650 MW at a capacity factor of 67%) equipped with an electrostatic precipitator (ESP), 100 kg/year of nickel is emitted into air (Rubin 1999). These nickel emissions are reduced to 16 kg/year for plants that are fitted with a wet lime/limestone flue gas desulfurization system downstream from the ESP. High-sulfur eastern coal has a higher nickel content than low-sulfur western coal, so power plants using eastern coal emit more nickel than those using western coal (QueHee et al. 1982).

It is estimated that in 1999, 570,000 tonnes of nickel were released from the combustion of fossil fuels worldwide (Rydh and Svärd 2003). Of this, 326 tonnes are released from electric utilities (Leikauf 2002).

From a public health point of view, the concentration of nickel associated with small particles that can be inhaled into the lungs is of greatest concern. The nickel content of aerosols from power plant emissions is not strongly correlated with particle size (Hansen and Fisher 1980). In one coal plant, 53 and 32% of nickel in emissions were associated with particles <3 and $<1.5 \mu\text{m}$ in diameter, respectively (Sabbioni et al. 1984). Other studies found that only 17–22% of nickel emissions from coal-fired power plants were associated with particles of $>2 \mu\text{m}$, and that the mass medium diameter (MMD) of nickel-containing particles from a plant with pollution control devices was $5.4 \mu\text{m}$ (Gladney et al. 1978; Lee et al. 1975). In one study, 40% of the nickel in coal fly ash was adsorbed on the surface of the particles rather than being embedded in the aluminosilicate matrix (Hansen and Fisher 1980). Surface-adsorbed nickel would be more available than embedded nickel.

Nickel emissions from municipal incinerators depend on the nickel content of the refuse and the design and operation of the incinerator. By comparing the nickel content of particles emitted from two municipal incinerators in Washington, DC, with that of atmospheric particulate matter, Greenberg et al. (1978) concluded that refuse incineration is not a major source of nickel in the Washington area. The average nickel concentrations in suspended particles from these incinerators ranged from 170 to 200 ppm. Nickel is not primarily associated with very fine or coarse particles. In tests performed under the Canadian National Incinerator Testing and Evaluation Program, 1.0 g nickel/ton refuse was emitted under

6. POTENTIAL FOR HUMAN EXPOSURE

normal operating conditions; when the combustion chamber operated at low and high combustion temperatures, nickel emissions increased to ≤ 2.2 g nickel/ton (Hay et al. 1986). These emissions can be compared with a factor of 0.33 g nickel/ton refuse obtained in a European study (Pacyna 1984). The European study also obtained an emission factor of 1.0 g nickel/ton for sewage sludge incineration.

An increase in nickel emissions over presettlement levels was assessed by dating and analyzing peat cores from a fen located in northern Indiana, which is downwind from the city of Chicago and the industrial complexes of Gary and East Chicago, areas that contain a large steel mill and a coal-fired power plant. The peak accumulation rate was 7.73 mg nickel/m²/year for 1970–1973, a factor of 21 greater than the accumulation rate in presettlement times (A.D. 1339–1656) (Cole et al. 1990).

Some work has been performed to determine the species of nickel present in air emissions from different source categories (EPA 1985a). This has been determined from analyses of dust by x-ray diffraction, scanning electron microscopy, and energy dispersive x-ray analysis or by an assessment of the reactions and transformations possible for the material present and the process conditions. Nickel resulting from oil combustion is primarily nickel sulfate with lesser amounts of complex metal oxides and nickel oxide. Approximately 90% of nickel in fly ash from coal combustion consists of complex (primarily iron) oxides. Nickel silicate and iron-nickel oxides would be expected from the mining and smelting of lateritic nickel ore, whereas nickel matte refining would produce nickel subsulfide and metallic nickel. The primary nickel species from secondary nickel smelting and steel and nickel alloys production is iron-nickel oxide.

6.2.2 Water

Nickel is a natural constituent of soil and is transported into streams and waterways in runoff either from natural weathering or from disturbed soil. Much of this nickel is associated with particulate matter. Nickel also enters bodies of water through atmospheric deposition.

Emission factors have been estimated for the release of trace metals to water from various source categories and these have been used to estimate inputs of these metals into the aquatic ecosystem. The global anthropogenic input of nickel into the aquatic ecosystem for 1983 is estimated to be between 33 and 194 million kg/year with a median value of 113 million kg/year (Nriagu and Pacyna 1988).

6. POTENTIAL FOR HUMAN EXPOSURE

Table 6-1 presents releases of nickel to water from facilities that produced, processed, and used nickel in 2001 in the United States. These releases, totaling 20,962 pounds (9,517 kg) of nickel, constitute 0.8% of environmental releases reported to TRI (TRI01 2003). Table 6-2 lists the releases of nickel compounds to water from facilities in the United States that produce, process, or use nickel compounds, according to the 2001 TRI (TRI01 2003). These releases, totaling 244,846 pounds (111,161 kg), constitute 0.5% of the environmental releases reported for nickel compounds in the TRI. The TRI data listed in Tables 6-1 and 6-2 should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

A survey of raw and treated waste water from 20 industrial categories indicated that nickel is commonly found in some waste waters. Those industries with mean effluent levels of $>1,000 \mu\text{g/L}$ in raw waste water were inorganic chemicals manufacturing (20,000 $\mu\text{g/L}$), iron and steel manufacturing (1,700 $\mu\text{g/L}$), battery manufacturing (6,700 $\mu\text{g/L}$), coil coating (1,400 $\mu\text{g/L}$), metal finishing (26,000 $\mu\text{g/L}$), porcelain enameling (19,000 $\mu\text{g/L}$), nonferrous metal manufacturing ($<91,000 \mu\text{g/L}$), and steam electric power plants (95,000 $\mu\text{g/L}$) (EPA 1981). Those industries with mean effluent levels $>1,000 \mu\text{g/L}$ in treated waste water were porcelain enameling (14,000 $\mu\text{g/L}$) and nonferrous metal manufacturing (14,000 $\mu\text{g/L}$) (EPA 1981). The maximum levels in treated discharges from these industries were 67,000 and 310,000 $\mu\text{g/L}$, respectively. In addition, four other industrial categories had maximum concentrations in treated discharges $>1,000 \mu\text{g/L}$. These were inorganic chemicals manufacturing (1,400 $\mu\text{g/L}$), iron and steel manufacturing (7,800 $\mu\text{g/L}$), aluminum forming (20,000 $\mu\text{g/L}$), and paint and ink formulation (80,000 $\mu\text{g/L}$).

Domestic waste water is the major anthropogenic source of nickel in waterways (Nriagu and Pacyna 1988). Concentrations of nickel in influents to 203 municipal waste water treatment plants (9,461 observations) ranged from 2 to 111,400 $\mu\text{g/L}$; the median value was $\approx 300 \mu\text{g/L}$ (Minear et al. 1981). From a study of influent streams of a waste water treatment plant in Stockholm, Sweden, it was determined that the waste streams from households (e.g., drinking water) and businesses (e.g., drinking water, car washes, chemical uses) account for 29% of nickel in influent streams (Sörme and Lagerkvist 2002). Another 31% of the nickel in influent streams is added at the waste water treatment plant through the addition of water treatment chemicals. Storm water accounts for between 1 and 5% of the nickel in influent streams. Concentrations in treated effluents were not reported. However, nickel may be removed by chemical precipitation or coagulation treatment in publicly owned treatment works, which reduces nickel releases (EPA 1981). For example, improvements in sewage treatment facilities have attributed to

6. POTENTIAL FOR HUMAN EXPOSURE

a reduction in the flux of nickel in waste water effluents into the Hudson River estuary, decreasing from 518 kg/day in 1974 to 43 kg/day in 1997 (Sañudo-Wilhelmy and Gill 1999)

Effluent water generated from mining and smelting operations comes from seepage, runoff from tailing piles, or from utility water used for mine operations. These discharges consist mostly of less-soluble silicates and sulfides and readily settle out. Tailing effluents from sulfidic ores are acidic due to the bacterial generation of sulfuric acid from the sulfidic minerals in the tailings, and very high concentrations of soluble nickel sulfate may be released. Tailing waters from the Onaping and Sudbury areas of Ontario, Canada, have an average nickel content of 42,500 µg/L, a factor of 8,300 greater than that found in river water (Mann et al. 1989). Since there is presently no nickel mining of sulfidic ore in the United States, nickel-containing waste water is not generated by this activity. However, past nickel mining may have contributed to nickel entering our waterways and accumulating in sediment. Old tailing piles may contribute to runoff for decades.

In the EPA-sponsored National Urban Runoff Program, in which 86 samples of runoff from 15 cities throughout the United States were analyzed, nickel was found in 48% of runoff samples, at concentrations of 1–182 µg/L (Cole et al. 1984). The geometric mean nickel concentration in runoff water from the cities studied was between 5.8 and 19.1 µg/L. In a more recent study of nickel concentrations in storm runoff water samples taken from different urban source areas (Table 6-3), the arithmetic means of the concentrations for dissolved nickel ranged from <1 to 87 µg/L, and from 17 to 55 µg/L for nickel that also included the metal associated with particulates (Pitt et al. 1995).

One of the potentially dangerous sources of chemical release at waste sites is landfill leachate. In a study that looked at leachate from three municipal landfills in New Brunswick, Canada, the results were conflicting. Average nickel concentrations in the three leachates (control) were 28 (45) µg/L, 33 (not detectable) µg/L, and 41 (23) µg/L (Cyr et al. 1987). Sediment at three sites below the leachate outfalls contained 11.9, 37.4, and 71.2 ppm of nickel (dry weight).

6.2.3 Soil

Most of the nickel released to the environment is released to land. Emission factors for nickel released to soil have been estimated for various industries (Nriagu and Pacyna 1988). These factors can be used to estimate industrial nickel releases to land. Excluding mining and smelting releases to land, 66% of estimated anthropogenic environmental releases or 325 million kg/year (median) are to soil (Nriagu and

6. POTENTIAL FOR HUMAN EXPOSURE

Table 6-3. Concentrations of Nickel Measured in Sheetflow Samples taken from Different Urban Source Areas in Birmingham, Alabama^a

Source area	Filtering ^b	Concentrations (µg/L)		
		Mean	Maximum	Minimum
Roof areas	NF	16	70	2.6
	F	<1	<1	<1
Parking areas	NF	45	130	4.2
	F	5.1	13	1.6
Storage areas	NF	55	170	1.9
	F	87	— ^c	— ^c
Street runoff	NF	17	70	1.2
	F	<1	<1	<1
Loading docks	NF	6.7	8.1	4.2
	F	1.3	— ^c	— ^c
Vehicle service area	NF	42	70	7.9
	F	31	— ^c	— ^c
Landscaping areas	NF	53	130	21
	F	2.1	— ^c	— ^c
Urban creeks	NF	29	74	<1
	F	2.3	3.6	<1
Detention ponds	NF	24	70	1.5
	F	3.0	6.0	<1

^a Pitt et al. 1995^b Nickel measured in either dissolved form (filtered, F) or associated with particulates (nonfiltered, NF).^c Nickel was detected in only one sample.

6. POTENTIAL FOR HUMAN EXPOSURE

Pacyna 1988). Some important sources of nickel released to soil are coal fly ash and bottom ash, waste from metal manufacturing, commercial waste, atmospheric fallout, urban refuse, and sewage sludge. Tables 6-1 and 6-2, which show the range of releases from industries listed in the TRI that produce, process, or use nickel, indicates that the bulk of nickel and nickel compounds is released to land. In 2001, 85.4% of the release of nickel or 2,480,253 pounds (1,126,034 kg) was to land (TRI01 2003). For nickel compounds, a higher percentage, 95.8% or 50,984,105 pounds (23,146,784 kg), was released to land in 2001 according to TRI (TRI01 2003). Underground injection accounted for 0.8% or 22,669 pounds (10,292 kg) of nickel and 1.8% or 980,689 pounds (445,233 kg) of nickel compounds released to the environment (TRI01 2003). Since not all facilities are required to report to the TRI, the list of facilities releasing nickel to land is not complete.

Based on 1999 production data, the equivalent of 0.6–3.3% of the nickel that was mined that year was used in the manufacture of portable batteries (Rydh and Svärd 2003). This amounts to approximately 17–31 ktons of nickel. Although current battery recycling programs in Europe claim success rates of upwards of 55%, the global recycling rates are typically lower, ranging between 5 and 50%. Therefore, on a global level, more than half of the nickel used in battery production will be disposed of in landfills and other waste sites.

6.3 ENVIRONMENTAL FATE

It is not always possible to separate the environmental fate processes relating to transport and partitioning from those relating to transformation for a metal and its various compounds and complexes. Because of analytical limitations, investigators rarely identify the form of a metal present in the environment. A change in the transport or partitioning of a metal may result from a transformation. For example, complexation may result in enhanced mobility, while the formation of a less-soluble sulfide would decrease its mobility in water. Adsorption may be the result of strong bonds being formed (transformation) as well as weak ones. Separating data relating to strong and weak adsorption in different sections is awkward and may not always be possible. Section 6.3.1 covers deposition and general adsorption of nickel, and Section 6.3.2 examines areas of environmental fate in which speciation occurs.

6.3.1 Transport and Partitioning

Nickel is released to the atmosphere in the form of particulate matter or adsorbed to particulate matter. It is dispersed by wind and removed by gravitational settling (sedimentation), dry deposition (inertial

6. POTENTIAL FOR HUMAN EXPOSURE

impaction characterized by a deposition velocity), washout by rain (attachment to droplets within clouds), and rainout (scrubbing action below clouds) (Schroeder et al. 1987). The removal rate and distance traveled from the source depends on source characteristics (e.g., stack height), particle size and density, and meteorological conditions.

Gravitational settling governs the removal of large particles ($>5\ \mu\text{m}$), whereas smaller particles are removed by other forms of dry and wet deposition. The partitioning between dry and wet deposition depends on the intensity and duration of precipitation, the element in question and its form in the particulate matter, and particle size. The importance of wet deposition relative to dry deposition generally increases with decreasing particle size. Removal of coarse particles may occur in a matter of hours. Small particles within the size range of $0.3\text{--}0.5\ \mu\text{m}$ may have an atmospheric half-life as long as 30 days and, therefore, have the potential to be transported over long distances (Schroeder et al. 1987). Evidence for the long-range transport of nickel is provided by the fact that emission sources in North America, Greenland, and Europe are responsible for elevated atmospheric nickel concentrations in the Norwegian Arctic during both the summer and winter (Pacyna and Ottar 1985).

Available studies indicate that nickel is broadly distributed among aerosol size groups. It has been concluded, based on the chemical and physical properties of atmospheric particles, that the concentrations of nickel in large particles ($>1\ \mu\text{m}$ diameter) that are commonly associated with particulates derived from natural sources are less than concentrations in smaller particles ($<1\ \mu\text{m}$ diameter) that are typically derived from anthropogenic sources (Giusti et al. 1993; Scudlark et al. 1994). For example, in a study to determine the size distribution of nickel-containing aerosols in clean, marine air was performed on an island in the German Bight (Stoessel and Michaelis 1986). The concentration of nickel in six size fractions increased with decreasing size from $\approx 0.3\ \text{ng}/\text{m}^3$ for particles $>7.2\ \mu\text{m}$ to $\approx 1.5\ \text{ng}/\text{m}^3$ for particles $<0.5\ \mu\text{m}$. However, experiments in Ontario showed that nickel is associated with relatively large particles, $5.6\pm 2.4\ \mu\text{m}$ (Chan et al. 1986). A 1970 National Air Surveillance Network study of the average nickel size distribution in six American cities indicated that the mass median diameter (MMD) is $\approx 1.0\ \mu\text{m}$ in all six cities (Lee et al. 1972). Although the sampling procedure used in this study may have underestimated large particles (Davidson 1980), it represents one of the few studies involving the size distribution of nickel aerosols in U.S. cities.

Metal deposition is characterized by large temporal and spatial variability. Deposition can be associated with precipitation (wet deposition) or result from processes such as gravitational settling of dust (dry deposition). Estimated nickel deposition rates range from 0.01 to 0.5 kg/hectare/year ($1\text{--}50\ \text{mg}/\text{m}^2/\text{year}$)

6. POTENTIAL FOR HUMAN EXPOSURE

and from 0.1 to 5.95 kg/hectare/year (10–595 mg/m²/year) in rural and urban areas, respectively (Schroeder et al. 1987). In the Florida Atmospheric Mercury Study (FAMS) conducted during 1993–1994, bulk deposition rates for nickel varied between 1.700 and 4.130 mg/m²/year, depending on local/regional anthropogenic activity (Landing et al. 1995). Nickel deposition from 1980 to 1981 in an industrial area of England where a number of ferrous and nonferrous metal smelting and manufacturing works were concentrated had a mean value of 8,800 ng/cm²/year (88 mg/m²/year), a factor of 8–25 above nonurban deposition rates (Pattenden et al. 1982). Wet deposition accounted for half of the deposition. Eighty-one percent of the nickel in rain was dissolved. Schroeder et al. (1987) reported the same percent of dry to wet deposition for nickel, whereas Chan et al. (1986) found that 2.2 times as much wet deposition as dry deposition occurred in Ontario in 1982 with little variability in the ratio across the province. The mean dry deposition rates for southern, central, and northern Ontario in 1982 were 0.25, 0.28, and 0.18 mg/m²/year, respectively. In southern Ontario, Canada, where the average concentration of nickel in rain was 0.557 ppb during 1982, 0.5 mg of nickel was deposited annually per square meter as a result of wet deposition (Chan et al. 1986). For central and northern Ontario, the mean concentrations of nickel in rain were 0.613 and 0.606 ppb, respectively, and the annual wet depositions averaged 0.5 and 0.4 mg/m². Wet and dry deposition of particulates emitted from the Claremont Incinerator in Claremont, New Hampshire, were measured within an area between 2 and 15 km from the incinerator. Wet deposition rates varied between 0.50 and 8.87 µg/m²/day (0.0005–0.00887 mg/m²/day) with a mean value of 3.0 µg/m²/day (0.003 mg/m²/day) and depended on distance from the incinerator and wind weight. The mean wet deposition rate of 3.0 µg/m²/day (0.003 mg/m²/day) was a factor of approximately 19 greater than the mean dry deposition rate of 0.16 µg/m²/day (0.00016 mg/m²/day), which had been calculated from values ranging from 0.067 to 0.29 µg/m²/day (0.000067–0.00029 mg/m²/day) (Feng et al. 2000).

Atmospheric deposition of nickel in coastal waters has been reported. Bulk and wet deposition of nickel into Massachusetts Bay was determined to be 7,200 and 3,000 µg/m²/year (Golomb et al. 1997), respectively, whereas a lower wet deposition rate of 257 µg/m²/year was measured for nickel in Chesapeake Bay (Scudlark et al. 1994). In Europe, a bulk deposition rate of 335 µg/m²/year was determined for nickel in the Severn Estuary in England (Golomb et al. 1997; Harrison et al. 1993) and a wet deposition rate of 880 µg/m²/year over the Dutch Delta (Nguyen et al. 1990). Atmospheric input of nickel into the Great Lakes has been estimated to average 160–590 ng/m²/year (Nriagu et al. 1996).

Wet and dry deposition of nickel into the world's oceans is estimated to be 8–11 and 14–17 gigagrams (10⁹ grams) per year, respectively (Duce et al. 1991). However, atmospheric deposition is only a minor contributor to the flow of nickel into the oceans and coastal waterways as compared to riverine and fluvial

6. POTENTIAL FOR HUMAN EXPOSURE

input of nickel. The nickel that is carried into oceans in both dissolved and particulate forms through riverine input is rated at 1,411 gigagrams per year, which is a factor of approximately 50 greater than the sum of the wet and dry deposition of nickel of 22–28 gigagrams per year (Duce et al. 1991). In an example of nickel input into Chesapeake Bay, the fluvial input of nickel of 98,700 kg/year (0.0987 gigagrams/year) is 25 times greater than bulk deposition of nickel from the atmosphere (Scudlark et al. 1994). However, for the Great Lakes the atmospheric input of nickel accounts for 60–80% of the total anthropogenic input of nickel into Lake Superior, and 20–70% of the total inputs into Lakes Erie and Ontario (Nriagu et al. 1996).

The fate of heavy metals in aquatic systems depends on partitioning between soluble and particulate solid phases. Adsorption, precipitation, coprecipitation, and complexation are processes that affect partitioning. These same processes, which are influenced by pH, redox potential, the ionic strength of the water, the concentration of complexing ions, and the metal concentration and type, affect the adsorption of heavy metals to soil (Richter and Theis 1980).

Much of the nickel released into waterways as runoff is associated with particulate matter; it is transported and settles out in areas of active sedimentation such as the mouth of a river. Additionally, when a river feeds into an estuary, the salinity changes may affect absorptivity due to complexation and competition for binding sites (Bowman et al. 1981). During a 4-month study of Lake Onondaga in Syracuse, New York, 36% of the nickel in the lake was lost to sediment (Young et al. 1982). Seventy-five percent of the nickel load into the polluted lake was soluble and remained in the lake. The soluble nickel is not likely to be as the Ni(II) ion, but is expected to exist as a complex. For example, in an analysis of the speciation of nickel in waste water effluents and runoff discharging into San Francisco Bay, it was found that approximately 20% of soluble nickel was complexed to moderately strong complexing agents, such as humic acid and biopolymers from activated sludges (Sedlak et al. 1997). However, a larger proportion of the nickel, 75% in waste water effluent and 25% in runoff, is found strongly complexed with stability constants that are similar to those found for synthetic chelating agents such as EDTA, DTPA, and phosphonates. Nickel is strongly adsorbed at mineral surfaces such as oxides and hydrous oxides of iron, manganese, and aluminum (Evans 1989; Rai and Zachara 1984). Such adsorption plays an important role in controlling the concentration of nickel in natural waters.

Nickel is strongly adsorbed by soil, although to a lesser degree than lead, copper, and zinc (Rai and Zachara 1984). There are many adsorbing species in soil, and many factors affect the extent to which nickel is adsorbed, so the adsorption of nickel by soil is site specific. Soil properties such as texture, bulk

6. POTENTIAL FOR HUMAN EXPOSURE

density, pH, organic matter, the type and amount of clay minerals, and certain hydroxides, as well as the extent of groundwater flow, influence the retention and release of metals by soil (Richter and Theis 1980).

Amorphous oxides of iron and manganese, and to a lesser extent clay minerals, are the most important adsorbents in soil. In alkaline soils, adsorption may be irreversible (Rai and Zachara 1984), which limits nickel's availability and mobility in these soils. For example, in recent studies of nickel speciation in ferromanganese nodules from loess soils of the Mississippi Basin, nickel is found to have a higher partition in the soil nodules than in soil clay matrices (Manceau et al. 2003). This is due to the selective sequestration of nickel by finely divided iron and manganese oxides in goethite and lithiophorite minerals present in the soils. Cations such as Ca^{2+} and Mg^{2+} have been reported to reduce adsorption due to competition for binding sites, whereas anions like sulfate reduce adsorption as a result of complexation. Nickel adsorption depends strongly on metal concentration and pH (Giusti et al. 1993). For each mole of nickel adsorbed by iron and manganese oxide, $\approx 1\text{--}1.5$ moles of hydrogen ions are released (Rai and Zachara 1984). For aluminum oxide, as many as 2.3 moles H^+ are released. Mustafa and Haq (1988) found that the adsorption of nickel onto iron oxide at pH 7.0 was rapid and increased with increasing temperature. They found that two hydrogen ions are released into a solution when nickel is adsorbed. These studies indicate that while Ni^{2+} is the predominant species in solution, NiOH^+ is preferentially adsorbed, and that both mono- and bidentate complexes may be formed with the iron/manganese/aluminum oxides.

Batch equilibrium studies were performed using seven soils and sediments spiked with varying concentrations of nickel to assess the potential mobility of nickel in contaminated subsoil (LaBauve et al. 1988). The range of Freundlich parameters $K(1/n)$, an adsorption constant, ranged from 739 (0.92) to 6,112 (0.87). One-, two-, and three-parameter models were used to evaluate the relation of soil properties and nickel retention. In the one-parameter model, pH was the best predictor. Cation exchange capacity (CEC) and iron oxide were the best predictors in the two-parameter models, and CEC, iron oxide, and percent clay were the best predictors in the three-parameter models. Nickel was more mobile in the soils than lead, cadmium, and zinc. The retention of nickel to two of the test subsoils diminished in the presence of synthetic landfill leachate, possibly because of complex formation. In another study in which batch adsorption experiments were conducted with a mixture of cadmium, cobalt, nickel, and zinc, and 38 different agricultural soils, taken from three depths at 13 sites, the adsorption constants ranged from 10 to 1,000 L/kg (Anderson and Christensen 1988). Soil pH, and to a lesser extent clay content and the amount of hydrous iron and manganese oxides, most influenced nickel sorption.

6. POTENTIAL FOR HUMAN EXPOSURE

In 12 New Mexican soils from agricultural areas and potential chemical waste disposal sites, Freundlich parameters $K (1/n)$ ranged from 8.23 to 650 (0.87–1.18); the median K was 388 (Bowman et al. 1981). The soil with the K of 8.23 was essentially unweathered rock that was not expected to have good adsorbing properties. The study concluded that most soils have an extremely high affinity for nickel and that once sorbed, nickel is difficult to desorb, which indicates covalent bond formation. Sadiq and Enfield (1984b) observed nickel ferrite formation following adsorption. Bowman et al. (1981) found that when nickel levels were >10 ppm, adsorption decreased. High concentrations of chloride decreased adsorption, but not as much as calcium ions, which indicates that calcium competition for sorbing sites is more important than chloride complexation for reducing adsorption. The presence of complexing agents, such as EDTA, dramatically lowers nickel adsorption, which has important implications at waste disposal sites if liquid nickel waste containing chelating agents is released to soil. Chelating agents that are added to soil containing adsorbed nickel appear to have a lesser effect.

The capacity of soil to remove nickel and the nature of the bound nickel were evaluated for 10 mineral and 3 organic soils from the southeastern United States (King 1988). Some soil samples were taken from the subsoil as well as the surface. The amount of adsorbed nickel ranged from 13 to 95%; the low value was found in subsoil, and the high value was found in soil high in organic matter. When extracted with potassium chloride, 5–87% of the nickel was nonexchangeable. Soil pH was the most important factor affecting sorbed and nonexchangeable nickel in all soil horizons. Both King (1988) and Tyler and McBride (1982) found much stronger nickel adsorptivity in organic soil than in mineral soils. Adsorption was improved by the quality and quantity of humus in the soil (Hargitai 1989). Nickel was enriched in humic and fulvic acids from Lake Ontario sediment (Nriagu and Coker 1980). It was estimated that 5–10% of the nickel in this sediment was bound to organic matter.

The leachability of nickel from some soils does not necessarily correlate with the total concentration of nickel in the soil. In an extraction study of soils sampled from the mining and smelting regions of Sudbury, Ontario, the percentage of nickel that is most easily extractable (in acetic acid) varied between 12 and 31% of the total nickel content (220–455 mg/kg) among the different sampling sites (Adamo et al. 1996). The remaining nickel was found in less extractable forms: 6–11% was found to be associated with manganese oxides and easily reducible iron oxides, 6–20% either bound to readily oxidizable organics or sulfides, and the remainder (55–73%) was associated with sulfides as separate grains or inclusions, iron oxide phases, carbon particles, and silicate spheroids. Similarly, in soils that are naturally enriched in heavy metals sampled from the Port MacQuaire region in Australia, the amount of nickel that can be easily extracted from soil samples is only a small fraction of the total nickel content (Lottermoser

6. POTENTIAL FOR HUMAN EXPOSURE

2002). Extraction of these soils with EDTA or acetic acid yielded leachable nickel which amounted to between <0.1–4.1 and <0.01%, respectively, of the total nickel concentrations in the soil samples. Use of stronger extraction methods, for example hydrochloric acid, yielded only leachable nickel in percentages (0.1–2.4%) equivalent to those found for EDTA. The low amount of acetic acid extractable nickel indicates negligible leaching of this metal from these soils into groundwater and surface waters (Lottermoser 2002).

Amendment of soils with exogenous humic acid reduces mobility of dissolved nickel in soil and also increases the bioavailability of this nickel to plants. Halim et al. (2003) showed that humic acid in soils from nickel-humic acid complexes results in the removal of dissolved and exchangeable nickel from soil water. The extractability of nickel increased with the aging time of the organic material. The increased bioavailability of nickel bound to humic acid is temporary and is thought to occur mainly as the result of preventing nickel from undergoing a transformation into insoluble species in soil.

Nickel (II) is poorly removed from waste water in the activated sludge process because of its high solubility (Stephenson et al. 1987). Only 30–40% of nickel was removed in a pilot activated sludge plant. Nickel removal in activated sludge plants is best correlated with effluent suspended solids (Kempton et al. 1987). Nickel is predominantly soluble in the effluent and is found complexed to humic acid, biopolymers, and other chelating agents (Sedlak et al. 1997).

In order to evaluate the potential of elements to leach from land-spread sewage sludge, Gerritse et al. (1982) studied the adsorption of elements to sandy and sandy loam top soils from water, salt solutions, and sludge solutions. They used metal levels that occurred in the solution phase of sewage sludge, 100–1,000 ppb in the case of nickel. The results indicated that nickel is fairly mobile in these soils; the adsorption constants were ≈ 10 –100 in the sandy soil and a factor of ≈ 10 higher in the sandy loam soil. The presence of sludge increases the mobility of nickel, particularly in sandy and sandy loam soils, which may be because of complexation with dissolved organic compounds (Kaschl et al. 2002) or increased ionic strength (Gerritse et al. 1982). However, land application of nickel-contaminated sludge did not give rise to increased levels of nickel in groundwater (Demirjian et al. 1984). Higher doses and repeated application of nickel-containing sewage sludge did not result in a proportional increase in nickel mobility (Hargitai 1989).

As part of EPA's National Runoff Program in Fresno, California, the soil water and groundwater at depths ≤ 26 m beneath five urban runoff retention/recharge basins were monitored during a 2-year study

6. POTENTIAL FOR HUMAN EXPOSURE

(Nightingale 1987). The results indicated that there were no significant downward movements of nickel with the recharge water.

Saline sediments from estuaries often contain pyrite and other readily oxidizable sulfur compounds. When these sediments are oxidized, such as when dredged sediment is exposed to oxygen, sulfuric acid may be produced, which may overwhelm the buffering capacity of the sediment, lower the pH (to pH 3.1 in a laboratory experiment), and dissolve the ferric oxides and hydroxides that entrap heavy metals (DeLaune and Smith 1985). As a result, significant amounts of nickel may be released from the dredged sediments. An analogous pH decrease following exposure to oxygen was not observed in freshwater sediment.

The presence of iron-(di)sulfides in wetland sediments has been associated with increased mobilization of nickel into groundwater during periods of drought in Holland (Lucassen et al. 2002). Dessication of sediments leads to oxidation of iron-(di)sulfides and subsequent acidification of the sediments. When the S/(Ca + Mg) ratios in these sediments rise above 2/3, mobilization of heavy metals like nickel occurs, leading to groundwater concentrations of nickel that exceeded the Dutch signal level of 50 ppb for nickel in 50% of the monitoring locations.

It has been reported that nickel is not accumulated in significant amounts by aquatic organisms (Birge and Black 1980; Zaroogian and Johnson 1984). The concentration of nickel in a major carnivorous fish in New York state, the lake trout, was the lowest, and the concentration did not increase appreciably with the age of the fish (Birge and Black 1980). The mean bioconcentration factor (BCF) for three carnivorous fish was 36. The concentration of nickel in mussels and oysters treated with 5 µg nickel/kg of seawater for 12 weeks averaged 9.62 and 12.96 µg nickel/g, respectively, on a dry weight basis (Zaroogian and Johnson 1984). When these data are adjusted for controls and the nickel concentration in tissue is expressed on a wet weight basis, the BCF for the mussels and oysters is ≈ 100 . After 2 weeks in flowing seawater, 58 and 38% of the tissue nickel was lost from the mussel and oyster, respectively. No significant loss of nickel occurred during the remainder of the 28-week depuration period. The content of acid volatile sulfide (AVS) in sediment helps determine the bioavailability of metals (Ankley et al. 1991). In studies of nickel and cadmium, the metals were toxic to an amphipod (*Hyallela azteca*) and an oligochaete (*Lumbriculus variegatus*) when the extracted metals/AVS ratio was >1 .

In the work of McGeer et al. (2003), bioconcentration factors (BCF) for nickel in various aquatic organisms (e.g., algae, arthropods, mollusks, and fish) was assessed based on whole-body metal

6. POTENTIAL FOR HUMAN EXPOSURE

concentrations and exposure concentrations that were obtained from the literature. For exposure concentrations within the range of 5–50 µg/L nickel in water, mean BCF values of 106 ± 53 (1 standard deviation [SD]) were obtained. When the authors also included data for exposure concentrations outside the range of 5–50 µg/L, a BCF value of 157 ± 135 was obtained. The authors noted that the BCF values were inversely correlated with the exposure concentrations, where the highest BCF values were obtained at the lowest exposure concentrations. There was no evidence that nickel biomagnifies in aquatic food webs and, in fact, there is evidence to indicate that the nickel concentrations in organisms decrease with increasing trophic level (McGeer et al. 2003; Suedel et al. 1994).

As part of the U.S. Geological Survey National Water-Quality Assessment (NAWQA) Program, there was no statistically significant correlation between nickel concentrations in bed-sediments collected from streams and rivers in both the Northern Rockies Intermontane Basin study area and the New Jersey study area, and nickel concentrations measured in liver and fillet samples taken from fish collected in the same study areas (USGS 2000a, 2000b). Also, nickel concentrations in fish liver and fillet samples were at or below the detection limits (<0.1 – 0.3 µg/g, dry weight) for nickel in these studies and are much lower than the concentrations of nickel measured in bed-sediments, which ranged from 12 to 43 µg/g (wet weight).

Uptake and accumulation of nickel into various plant species is known to occur. For example, Peralta-Videa et al. (2002) report the accumulation of nickel in alfalfa grown from soils contaminated with a mixture of four metals (e.g., Cd(II), Cu(II), Ni(II), and Zn(II)) at a loading of 50 mg/kg for each metal. Concentration ratios of nickel in plant versus soil (based on dry weights) ranged between 22 and 26 over a pH range of 4.5–7.1. As with most plant species that hyperaccumulate metals, the alfalfa actively removes and translocates heavy metals, like nickel, from the roots to the shoots.

Two studies concerning levels in voles and rabbits living on sludge-amended land did not indicate any accumulation of nickel in these herbivores or in the plants they fed upon (Alberici et al. 1989; Dressler et al. 1986). The lack of significant bioaccumulation of nickel in aquatic organisms, voles, and rabbits indicates that nickel is not biomagnified in the food chain.

6.3.2 Transformation and Degradation

Analytical methods do not generally allow identification of the precise form of nickel present in environmental samples or an assessment of the transformations that may occur. Sequential extraction techniques are sometimes employed to determine how tightly nickel is bound to particles or in

6. POTENTIAL FOR HUMAN EXPOSURE

environmental matrices. Using different and progressively stronger extracting agents, the fractions of a sample that are exchangeable, adsorbed, easily reducible, moderately reducible, or organically bound carbonates, sulfides, and residual can be determined (Rudd et al. 1988; Rybicka 1989).

6.3.2.1 Air

Little is known about the chemical forms and physical and chemical transformations of trace elements in the atmosphere primarily because analytical methods provide information concerning the metal content rather than the specific compounds or species. In the absence of specific information, it is generally assumed that elements of anthropogenic origin, especially those emanating from combustion sources are present as the oxide, and nickel oxide has been identified in industrial emissions (Schroeder et al. 1987). Windblown dust particles may contain nickel in mineral species, which often contain nickel as the sulfide. Increases in the concentration of nickel in Sequoia National Park in California during rain coming from the south correlated with a sharp (7–13 times greater concentration) increase in sulfate (Cahill 1989). Nickel sulfate is a probable atmospheric species resulting from the oxidation of nickel in the presence of sulfur dioxide (Schmidt and Andren 1980).

The form of nickel in particles from different industries varies. The mineralogical composition, chemical content, and form of dusts from nine industries in Krakow, Poland, were examined (Rybicka 1989). The chemical form of a particle-associated heavy metal that was assessed by a five-step extraction scheme classified the metal as exchangeable, easily reducible (manganese oxides, partly amorphous iron oxyhydrates and carbonates), moderately reducible (amorphous and poorly crystallized iron oxyhydrates), organically bound or sulfidic, and residual. Dusts from power plants had a silicate characteristic with quartz and mullite predominant. Approximately 90% of the nickel from these facilities was in the residual fraction. Only 40–60% of the nickel from metallurgical, chemical, and cement plants was in the residual fraction. Essentially none of the nickel from any of the industries was in an organic/sulfidic fraction. Dusts from metallurgical, chemical, and cement plants contained between 0 and 10% (typically 5%) of the nickel in the relatively mobile, cation-exchangeable fraction. Thirty percent of the nickel in dust from a slag processing facility was in this form.

6.3.2.2 Water

In natural waters, nickel primarily exists as the hexahydrate. While nickel forms strong, soluble complexes with OH^- , SO_4^{2-} , and HCO_3^- , these species are minor compared with hydrated Ni^{2+} in surface

6. POTENTIAL FOR HUMAN EXPOSURE

water and groundwater with pH <9 (Rai and Zachara 1984). Under anaerobic conditions, such as may exist in deep groundwater, nickel sulfide would reduce free aqueous nickel concentrations to low levels.

Precipitation can remove soluble nickel from water. In aerobic waters, nickel ferrite is the most stable compound (Rai and Zachara 1984). Nickel may also be removed by coprecipitation with hydrous iron and manganese oxides. Nickel removed by precipitation and coprecipitation settles into the sediment.

Nickel in sediment may be strongly bound or present in a removable form. A metal's form in soil or sediment and its availability are determined by measuring the extractability of the metal with different solvents. Sediment samples from western Lake Ontario were analyzed in regard to the compositional associations of nickel by a series of sequential extractions (Poulton et al. 1988). The mean nickel percentages in the various fractions were as follows: exchangeable, 0.7 ± 1.4 ; carbonate, 0.0; iron or manganese oxide-bound, 0.0; organic-bound, 7.4 ± 4.1 ; and residual, 91.9 ± 4.5 . The nickel concentration in 450 uncontaminated estuarine and coastal marine sites in the southeastern United States covaried significantly with the aluminum concentration, suggesting that natural aluminosilicates are the dominant natural metal-bearing phase in some aquatic systems (Windom et al. 1989). In 13 random samples of bottom sediment from the highly industrialized Meuse River in The Netherlands, between 0 and 88% (median 33%) of the nickel was removable at low pH, showing the great variability of nickel to adsorb to sediments (Mouvet and Bourg 1983).

Nickel removed by coprecipitation can be remobilized by microbial action under anaerobic conditions (Francis and Dodge 1990). Remobilization results from enzymatic reductive dissolution of iron with subsequent release of coprecipitated metals. A lowering of pH as a result of enzymatic reactions may indirectly enhance the dissolution of nickel. Experiments using mixed precipitates with goethite (α -FeOOH) indicated that a *Clostridium* species released 55% of the coprecipitated nickel after 40 hours. Similarly, precipitated nickel sulfides in sediment can be mobilized through sulfur oxidation by *Thiobacilli* (Wood 1987). In this case, the oxidized sulfur may produce H_2SO_4 and decrease the pH.

6.3.2.3 Sediment and Soil

An analysis of the thermodynamic stability models of various nickel minerals and solution species indicates that nickel ferrite is the solid species that will most likely precipitate in soils (Sadiq and Enfield 1984a). Experiments on 21 mineral soils supported its formation in soil suspensions following nickel adsorption (Sadiq and Enfield 1984b). The formation of nickel aluminate, phosphate, or silicate was not

6. POTENTIAL FOR HUMAN EXPOSURE

significant. Ni^{2+} and $\text{Ni}(\text{OH})^+$ are major components of the soil solution in alkaline soils. In acid soils, the predominant solution species will probably be Ni^{2+} , NiSO_4 , and NiHPO_4 (Sadiq and Enfield 1984a).

A large percentage of nickel in sewage sludges exists in a form that is easily released from the solid matrix (Rudd et al. 1988). Although the availability of nickel to plants grown in sludge-amended soil is correlated with soil-solution nickel, it is only significantly correlated with DTPA-extractable nickel (Adams and Kissel 1989).

6.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

6.4.1 Air

Mean ambient air concentrations of nickel typically range between 6 and 20 ng/m^3 and can be high as 150 ng/m^3 near anthropogenic sources of airborne nickel (Barceloux 1999). Schroeder et al. (1987) reported nickel concentrations in particulate matter in the U.S. atmosphere of 0.01–60, 0.6–78, and 1–328 ng/m^3 in remote, rural, and urban areas, respectively. Nickel concentrations in particulate matter ($\text{PM}_{2.5-8}$), collected in Spokane, Washington, from January 1995 to March 1999, averaged 1.2 ± 0.9 (1 SD) ng/m^3 (Claiborn et al. 2002). Based on emission data contained in the EPA 1996 NTI database, an average concentration of nickel in ambient air in the contiguous United States was estimated to be 2.22 ng/m^3 (median concentration = 0.948 ng/m^3) (EPA 2003u). The five states with the highest average concentrations of nickel in ambient air were (ng/m^3): West Virginia (6.60), Utah (4.42), Delaware (4.10), New York (3.80), and Pennsylvania (3.69); the five states with the lowest concentrations were: Wyoming (0.127), South Dakota (0.157), North Dakota (0.211), Montana (0.311), and Vermont (0.311). Annual mean nickel concentrations in 11 Canadian cities measured during 1987–1990 ranged from 1 to 20 ng/m^3 , while at a rural location the mean nickel concentration was 1 ng/m^3 (CEPA 1994). In another Canadian study, mean exposure concentrations for nickel in air for residents living near copper smelters and refineries and zinc plants ranged between 0.005 and 0.151 $\mu\text{g}/\text{m}^3$ (5–151 ng/m^3) in comparison to background levels of 0.00069 $\mu\text{g}/\text{m}^3$ (0.69 ng/m^3) (Newhook et al. 2003). Annual average nickel concentrations at three remote sites in the arctic region of Canada ranged from 0.14 to 0.45 ng/m^3 (Barrie and Hoff 1985). Levels of nickel and other anthropogenic species peaked during January and February, possibly indicating the significance of combustion sources. Nickel levels in the air at three native villages in northern Alberta, Canada, were 0.779 ± 0.774 , 1.1 ± 0.57 , and 4.97 ± 9.2 ng/m^3 , indicating that air concentrations of nickel can be highly variable (Moon et al. 1988).

6. POTENTIAL FOR HUMAN EXPOSURE

According to the EPA's National Air Surveillance Network (NASN) report for 1977, 1978, and 1979, median nickel concentrations were below the detection limit for urban and nonurban samples except for 1978; during 1978, the urban median was 6 ng/m³ (Evans et al. 1984). The detection limit for inductively-coupled-plasma atomic emission spectroscopy (ICP-AES), the method used in the EPA study, was 1 ng/m³ (EPA 1986a; Evans et al. 1984). In the EPA study, 10,769 urban samples and 1,402 nonurban 24-hour air samples were analyzed. Five percent of the urban samples were >33, 32, and 30 ng nickel/m³ for 1977, 1978, and 1979, respectively; 5% of the nonurban samples were >10, 10, and 6 ng/m³, respectively, for these 3 years. Ninety-nine percent of the urban and nonurban samples for these 3 years did not exceed 68 and 52 ng/m³, respectively (Evans et al. 1984). Combined urban and nonurban measurements for the 99th percentile from the NASN (1977–1979) and its successor, the National Air Monitoring Filter Sites (NAMFS) (1980–1982), showed a sharp decline from 62 and 67 ng/m³ in 1977 and 1978 to 23 and 30 ng/m³ in 1981 and 1982. Mean levels for the combined urban and nonurban sites over the 6-year period ranged from 7 to 12 ng/m³ (EPA 1986a). According to the NASN data for 1965–1968, the average atmospheric nickel concentration in the air of 28 cities ranged from 3 to 90 ng/m³, with an overall average of 26 ng/m³ (NAS 1975). These data suggest that atmospheric nickel concentrations in the United States have been declining. No reason for this downward trend was suggested (EPA 1986a).

The most intensive study of the nickel concentration in the United States was the result of analyzing air samples collected during 1968–1971 for use in a lead survey (Saltzman et al. 1985). This study is significant because numerous sites in four cities were analyzed continuously over 1 year and analyzed by a single, highly experienced laboratory. Samples from 33 sites in Chicago, Houston, New York, and Washington, DC, were analyzed for nickel resulting in respective geometric mean nickel concentrations of 15, 18, 23, and 42 ng/m³. The results for Washington, DC, are in basic agreement with the results obtained from Kowalczyk et al. (1982). In this study, 24-hour samples collected at 10 locations yielded average nickel concentrations ranging from 5.7 to 35 ng/m³, with a mean concentration of 17 ng/m³. The two major contributing sources are believed to be oil and coal combustion. The enrichment factor for nickel over crustal levels in 29 cities is 11 (Gladney et al. 1984). An enrichment factor considerably >1 indicates that the source of an element is anthropogenic. In Houston, the average concentration of nickel in both the fine (0.1–2.5 µm) aerosols and those >2.5 µm was 4±1 ng/m³ (Johnson et al. 1984).

As part of the Airborne Toxic Element and Organic Substances project for determining patterns of toxic elements in different settings, three urban areas (Camden, Elizabeth, and Newark) and one rural site

6. POTENTIAL FOR HUMAN EXPOSURE

(Ringwood) in New Jersey were studied during two summers and winters between 1981 and 1983 (Lioy et al. 1987). Each site was sampled every 24 hours for 39 consecutive days. The geometric mean nickel concentrations were 8.0–34.0, 5.0–28.0, 10.0–27.0, and 5.0–13.0 ng/m³ for Camden, Elizabeth, Newark, and Ringwood, respectively. The nickel levels measured in the industrial urban areas may be compared to the arithmetic mean values reported in the National Air Surveillance survey (9.6–11.0 ng/m³) for 1977–1979 (Evans et al. 1984). Summer and winter maxima in the three urban areas ranged from 24.0 to 39.0 and from 81.0 to 112.0 ng/m³, respectively, and 22.0 and 32.0 ng/m³, respectively, for Ringwood.

The first and second highest annual average nickel concentrations in the air in Texas between 1978 and 1982, according to the Texas Air Control Board, were 49 and 34 ng/m³ at Port Arthur and Beaumont, respectively (Wiersema et al. 1984). The statewide 1978–1982 average was 1 ng/m³. Mean nickel levels showed relatively little geographic variation in Ontario where concentrations in southern, central, and northern Ontario were 0.81, 0.91, and 0.58 ng/m³, respectively (Chan et al. 1986).

Voutsas and Samara (2002) report elevated concentrations of nickel in particulate matter (PM_{7.2}) collected near industrial sites within the greater Thessaloniki (Greece) area during the time period summer 1997 through summer 1998. The mean (± 1 SD) concentration of nickel in particulate matter collected at three industrial sites (e.g., Pb and Zn smelters, non-ferrous metal industries, iron and steel manufacturing, etc.) of 12.8 (± 8.2) ng/m³ was statistically greater than the mean concentration of 6.8 (± 5.3) ng/m³ for nickel measured in PM_{7.2} collected at three urban sites.

Nickel concentrations in particulate matter PM₁₀ was measured at three Midwestern sites, two urban sites with a large industrial component and one rural site, in samples collected from September 1985 to June 1988 (Sweet et al. 1993). Nickel concentrations in the fine PM₁₀ particles (<1–2.5 μ m) taken from collection sites in East St. Louis and Southeast Chicago averaged 2.1 \pm 1.4 (1 SD) and 2.7 \pm 2.6 ng/m³, respectively, and were similar to those measured in the coarser PM₁₀ particles (2.5–10 μ m) of 1.8 \pm 1.5 and 2.1 \pm 1.0 ng/m³, respectively. The concentrations of nickel measured in both the fine and coarse particles collected at the East St. Louis and Southeast Chicago sites were higher than the average concentration of nickel of 0.5 \pm 0.3 and 0.7 \pm 0.5 ng/m³ measured in fine and coarse particles, respectively, collected from a rural site (Bondville, Illinois). The higher concentrations of nickel in the East St. Louis and Southeast Chicago sites are attributed to emissions from zinc smelters and steel mills/oil combustion, respectively.

Nickel concentrations in indoor air are generally <10 ng/m³. In a study of 10 homes in the southeast Chicago area, indoor and outdoor air samples were regularly sampled between June 1994 and April

6. POTENTIAL FOR HUMAN EXPOSURE

1995 (van Winkle and Scheff 2001). Of the 48 samples taken, 35 had nickel concentrations above the detection limit of the assay with a mean (± 1 SD) concentration of $0.002 \pm 0.002 \mu\text{g}/\text{m}^3$ and a maximum value of $0.008 \mu\text{g}/\text{m}^3$. The median indoor nickel concentration of $0.003 \mu\text{g}/\text{m}^3$ was similar to the median outdoor nickel concentration of $0.0034 \mu\text{g}/\text{m}^3$. Indoor air samples taken from 394 homes in Suffolk and Onondaga Counties of New York state contained nickel concentrations that were similar to those found in the Chicago study (Koutrakis et al. 1992). A mean indoor nickel concentration of $2 \text{ ng}/\text{m}^3$ ($0.002 \mu\text{g}/\text{m}^3$) was derived from a sampling 28 homes. The New York study also examined nickel concentrations in indoor air as a function of combustion sources within the home (e.g., resident smoker, wood-burning stove, kerosene heater) and found no difference in the mean nickel concentrations between homes containing these combustion sources and homes without. In a study of 46 high school students in New York City conducted in the winter and summer of 1999, the concentrations of nickel in collected particulates ($\text{PM}_{2.5}$) to which these students were exposed was assessed using personal monitoring devices and stationary measurements of airborne nickel both within and outside the home (Kinney et al. 2002). The mean (± 1 SD) air concentrations of nickel obtained from the outdoor, indoor and personal monitors measured during the winter survey period were similar (32.3 ± 22.4 , 31.6 ± 54.5 , and $49.6 \pm 114 \text{ ng}/\text{m}^3$, respectively). Likewise, the mean nickel concentrations obtained from all three monitors during the summer survey period were also found to be similar (11.7 ± 6.3 , 12.6 ± 8.4 , and $17.3 \pm 24.7 \text{ ng}/\text{m}^3$, respectively), although somewhat lower than the winter concentrations. These results suggest that ambient concentrations of nickel are the dominating force in determining both indoor and personal exposures to nickel.

6.4.2 Water

Surface water contains low nickel levels. Uncontaminated freshwater and seawater typically contain about $300 \text{ ng}/\text{L}$ of nickel (Barceloux 1999). The concentration in seawater ranges from 100 to $3,000 \text{ ng}/\text{L}$ nickel/L. Higher levels are found in deeper waters than in surface water (Mart et al. 1984; Sunderman 1986; van Geen et al. 1988; Yeats 1988). Water from the surface of the Atlantic Ocean, deep within the Atlantic Ocean (400 m), and the Atlantic shelf contained 1.8 nM ($106 \text{ ng}/\text{L}$), 2.7 nM ($158 \text{ ng}/\text{L}$), and 3.5 nM ($205 \text{ ng}/\text{L}$) nickel, respectively (van Geen et al. 1988). Helmers and Schrems (1995) reported a concentration of $50 \text{ ng}/\text{L}$ for nickel in surface waters in the equatorial Atlantic Ocean. The mean value of nickel in surface water of the eastern Arctic Ocean is $126 \pm 54 \text{ ng}/\text{L}$ (Mart et al. 1984). Deep water samples taken at 1,500 and 2,000 m contained higher levels of nickel (220 and $230 \text{ ng}/\text{L}$, respectively). Nickel concentrations in surface water transected on a cruise from Nova Scotia to the Sargasso Sea ranged from 117 to $329 \text{ ng}/\text{L}$, with a median concentration of $200 \text{ ng}/\text{L}$ (Yeats 1988). Concentrations

6. POTENTIAL FOR HUMAN EXPOSURE

were ≈ 2 times higher in deep water. The nickel levels reported in the North Pacific and Pacific Antarctic were somewhat higher. Nickel concentration in surface water decreased by a factor of approximately 2 with increases in percent salinity from approximately 30 to 36‰ and increased with increasing phosphorus concentration. Nickel concentrations in South San Francisco Bay were about 3,000 ng/L, with one-third to one-half of the nickel complexed to a class of strong organic ligands (Donat et al. 1994).

The nickel content of fresh surface water has been reported to average between 15 and 20 μg nickel/L (Grandjean 1984; NAS 1975). The concentration of dissolved nickel in the lower Mississippi River ranged from 1.2 to 1.5 μg /L in seven samples taken at different flow conditions (Shiller and Boyle 1987). In a 1977–1979 study of representative groundwaters and surface waters throughout New Jersey, in which >1,000 wells and 600 surface waters were sampled, the median nickel levels in groundwater and surface water were both 3.0 μg /L (Page 1981). The respective 90 percentile and maximum levels were 11 and 600 μg /L for groundwater and 10 and 45 μg /L for surface water. The nature of the sites with elevated nickel levels was not indicated. However, groundwater polluted with nickel compounds from a nickel-plating facility contained as high as 2,500 μg /L (IARC 1990). Nickel concentrations were measured in 30 groundwater samples taken from the South Platte River alluvial aquifer underlying Denver, Colorado (Bruce and McMahon 1996). The samples represented a variety of land-use activities, including commercial, industrial, residential, and agricultural. A median nickel concentration of 3 μg /L was determined, with maximum and minimum concentrations values of 20 and 1 μg /L, respectively.

Nickel concentrations from five stations in Lake Huron in 1980 had median and maximum nickel concentrations of 0.54 and 3.8 μg /L, respectively (Dolan et al. 1986). In a 1982 survey, nickel concentrations in Hamilton Harbor, Lake Ontario, ranged from <1 to 17 μg /L, with a median of 6 μg /L (Poulton 1987). The median nickel concentration from an analogous 1980 survey was 4 μg /L. Suspended sediment in surface samples (0.2 m) at Hamilton Harbor, Lake Ontario, contained 17–23 ppm nickel; samples from a depth of 20 m contained 67–87 ppm, similar to the 66 ppm of nickel found in bottom sediment samples (Poulton 1987). These findings suggest that resuspension of bottom sediment is a major contributor to the suspended sediment at 20 m depth. In a 1993 survey of heavy metal concentrations in the Great Lakes, average nickel concentrations of 872 and 752 ng/L were measured in Lakes Erie and Ontario, respectively (Nriagu et al. 1996). Concentrations were highest in near-shore waters due to their proximity to urban centers and polluted river mouths. A decrease in the average concentration of nickel measured in Lake Ontario, from 838 ng/L measured in May/June to a value of 751 ng/L obtained in October, indicates that sedimentation of suspended particles results in a fast depletion of nickel during the summer stratification (Nriagu et al. 1996).

6. POTENTIAL FOR HUMAN EXPOSURE

Tap water that is used for drinking purposes generally contains nickel at concentrations ranging from 0.55 to 25 µg/L, in the United States (FDA 2000; O'Rourke et al. 1999; Thomas et al. 1999). Nickel concentrations in tap water measured in the Total Diet Study 1991–1999 ranged from 0 to 0.025 mg/kg (\approx 0–25 µg/L) with a mean value of 0.002 mg/kg (\approx 2 µg/L) (FDA 2000). Analysis of data obtained during 1995–1997 from the National Human Exposure Assessment Study (NHEXAS) yielded median concentrations of nickel in tap water (used as drinking water) of 4.3 µg/L (10.6 µg/L, 90% percentile) in the Arizona study and 4.0 µg/L (11 µg/L, 90% percentile) in the EPA Region 5 (Illinois, Indiana, Michigan, Minnesota, Ohio, and Wisconsin) study (O'Rourke et al. 1999; Thomas et al. 1999). Mean levels for nickel in European drinking water range from 1 to 11 µg/L (Andersen et al. 1983; Barceloux 1999; Dabeka 1989; IARC 1990). In a 1969–1970 survey of 969 water supplies in the United States representing all water supplies in eight metropolitan areas and one state (2,503 samples), 21.7% of samples had concentrations <1 µg/L, 43.2% of the samples contained between 1 and 5 µg nickel/L, 25.6% of the samples contained between 6 and 10 µg nickel/L, 8.5% of the samples contained between 11 and 20 µg nickel/L, and 1% had levels >20 µg nickel/L (NAS 1975). In a national survey of raw, treated, and distributed water from 71 municipalities across Canada, the median nickel concentration in both treated and distributed provincial drinking water were \leq 0.6–1.3 µg/L for treated water and 1.8 µg/L for distributed water (Meranger et al. 1981). The maximum value was 72.4 µg/L from Sudbury, Ontario. The similarity between median and maximum values for treated and distributed water suggests that nickel is not generally picked up in the distribution system. An exception is in Quebec where the maximum nickel concentration increased from 8.3 to 22.0 µg/L between the treated and distributed water. The median nickel levels in the provincial raw water ranged from \leq 0.6 to 2.3 µg/L. The maximum levels in tap waters from British Columbia, Prince Edward Island, the Yukon, and Northwest Territories were below the detection limit. The similarity in values between raw and treated water indicates that treatment methods (mainly treatment with lime, alum, or soda ash) did not remove nickel effectively.

Elevated nickel levels may exist in drinking water as a result of the corrosion of nickel-containing alloys used as valves and other components in the water distribution system as well as from nickel-plated or chromium-nickel-plated faucets. In a Seattle study, mean and maximum nickel levels in standing water were 7.0 and 43 µg/L, respectively, compared with 2.0 and 28 µg/L in running water (Ohanian 1986). A similar result was observed in a comparison of the mean (\pm 1 standard deviation) and 90th percentile concentrations of nickel measured during the NHEXAS EPA Region 5 study in standing tap water of (9.2 [\pm 21] and 16 µg/L) and in tap water sampled after the water line had been flushed for 3 minutes (5.3 [\pm 4.4] and 11 µg/L) (Thomas et al. 1999). Even if an individual was to consume only first draw

6. POTENTIAL FOR HUMAN EXPOSURE

water (containing nickel at the maximum concentration [48 µg/L] obtained from the Seattle study) as their sole source of drinking water, their daily intake of 86 µg/day is still less than the lifetime daily limit of 100 µg/day (Table 8-1) set by EPA, assuming the consumption of 2 L/day (EPA 2000). Although leaching of metals from pipes generally increases with decreasing pH, none of the nickel studies reported the pH of the tap water. First water drawn from hot water taps plated with nickel may contain concentrations as high as 1–1.3 mg/L (Barceloux 1999). Andersen et al. (1983) reported nickel concentrations in standing water sampled from hot or cold water taps in 35 flats located in Denmark, and 46 locations in Sweden and 10 other European cities. Nickel concentrations in standing water drawn from hot water taps ranged between 5 and 490 µg/L; nickel concentrations in standing water drawn from cold water taps ranged between 5 and 75 µg/L.

Nickel concentrations were measured as part of a study of heavy metal content in streams and creeks, located in the Black Hills of South Dakota that are impacted by abandoned or active mining operations (May et al. 2001). The concentrations of nickel in these surface waters generally ranged between 1.3 and 7.6 µg/L and were typically highest near where they received drainage water from abandoned or active mining operations. At one location, nickel concentrations as high as 20 µg/L were determined and were attributed to effluent and entrained streambed tailings from previous mining activities. The concentrations of nickel in water did not correlate with the concentrations of nickel in the underlying sediments.

Several investigators reported the presence of nickel concentrations in rain. The annual mean nickel concentration in precipitation at Lewes, Delaware, was 0.79 µg/L (Barrie et al. 1987). The mean concentration (\pm standard deviation) of nickel collected from rain showers in southern Ontario, Canada, in 1982 was 0.56 ± 0.07 µg/L (Chan et al. 1986). The mean concentrations in northern and central Ontario were both 0.61 µg/L, indicating a lack of spatial variability. Sudbury, the site of a large nickel smelter, is located in central Ontario. Rainwater samples collected near two nickel smelters and one ore roaster in northwestern Russia, located near the Finnish and Norwegian borders, had median nickel concentrations ranging between 1.31 and 57 µg/L with values as high as 132 µg/L (Reimann et al. 1997). The differences observed in the concentration of nickel in rainwater between the three sites roughly correlated with the reported emission rates for nickel into air from these sites. Background measurements of nickel in rainwater sampled several hundred kilometers from these industrial sites had median values ranging between 0.09 and 0.21 µg/L. Nickel concentrations from rain samples collected at four sites in Sweden had a mean range of 0.017–0.51 µg/L (Hansson et al. 1988). The nickel concentration in rainwater collected near a large municipal incinerator in Claremont, New Hampshire, was measured at a mean value

6. POTENTIAL FOR HUMAN EXPOSURE

of 0.69 µg/L (Feng et al. 2000). Nickel concentrations in rain collected between 1985 and 1990 from remote regions of the Atlantic Ocean ranged from 0.63 to 1.42 µg/L (Helmerts and Schrems 1995). The concentration of nickel in cloud water sampled on the Olympic Peninsula of Washington state in May 1993 was measured at 0.5±0.4 µg/L; the air-equivalent concentration is 0.2 ng/m³ (Vong et al. 1997).

Nickel in snow from Montreal, Canada, was highly enriched compared with ambient air, ranging from 2 to 300 ppb (Landsberger et al. 1983). The nickel content of snow particulate matter was 100–500 ppb. Nickel concentrations were highly correlated with those of vanadium, suggesting that oil combustion was a source. The nickel concentration in snow collected near a large municipal incinerator in Claremont, New Hampshire, was measured at a mean value of 0.62 µg/L (Feng et al. 2000). Snow samples were collected several hundred kilometers from the nearest known nickel emission sources (e.g., smelters and ore processing facilities) in northwestern Russia, near the Finish and Norwegian borders. Mean nickel concentrations of 0.0019 mg/L (1.9 µg/L) were measured in the snow melt or, based on the volume of accumulated snow, 0.26 mg/m³ (Kashulin et al. 1997).

6.4.3 Sediment and Soil

Sediment is an important sink for nickel in water. Mean nickel levels in pristine sediment from five sites off the northern coast of Alaska ranged from 25 to 31 ppm (Sweeney and Naidu 1989). Of this amount, ~10% was extractable. Nickel was most highly associated with silt and clay. Background nickel concentrations in sediment cores from open water of Lake St. Clair ranged from 8.5 to 21.1 ppm, with mean concentrations of 13.6 and 17.6 ppm in sand and silty clay sediment, respectively (Rossmann 1988). The average nickel concentrations in surface sediment of four Rocky Mountain lakes ranged from 9.6 to 18 ppm (dry weight). The nickel concentrations of the five other lakes reported in the literature ranged from 6.4 to 38 ppm (Heit et al. 1984). Nickel concentrations measured in the sediments taken in 1998 from the Clark, Fork-Pend, and Spokane river basins in the region adjoined by the states of Washington, Idaho, and Montana ranged from 12 to 27 µg/g, dry weight (USGS 2000).

The range and mean nickel levels in surface sediment of Penobscot Bay, Maine, were 8.22–35.0 and 26.6 ppm (dry weight), respectively (Larsen et al. 1983). This is higher than the levels found at cleaner sites in Casco Bay in the Gulf of Maine (17.6 ppm) and Eastern Long Island (7.6 ppm) (Larsen et al. 1983). As part of the Long Island-New Jersey National Water-Quality Assessment (LINJ-NAWQA) Program, nickel concentrations were measured in bed-sediments taken from streams and rivers in New Jersey in the fall of 1997 (USGS 2000b). A median nickel concentration of 30 µg/g (wet weight) was

6. POTENTIAL FOR HUMAN EXPOSURE

determined in bed-sediments, with values ranging from 18 to 43 µg/g. In a similar NAWQA study of the Northern Rockies Intermontane Basins study area, a median nickel concentration in bed-sediments of 18 µg/g (wet weight) was determined, with a range of values of 12–24 µg/g (USGS 2000a). Rice (1999) gives a summary of trace metal concentrations in 541 bed-sediment samples taken from throughout the conterminous United States as part of the NAWQA study, reporting a median nickel concentration of 27 µg/g, with a larger range of values 6–530 µg/g than found from the results of the separate NAWQA studies noted above. Nickel is more highly associated with fine-grained sediment with a higher organic carbon content. Levels reflect anthropogenic input as well as mineralization of the regional bedrock.

Nickel content in sediments is expected to be high near sources of nickel emissions. For example, Lake Kuetsjärvi is located approximately 1 km from the large Pechenganickel nickel smelter in northwestern Russia and receives both airborne and waste water emissions from the plant (Lukin et al. 2003).

Sediment core samples taken from the lake, with nickel measurements, were acquired from the top 1 cm surface of the core (current status) and at a core depth of 20–30 cm (background). The average nickel concentrations determined for surface layer and background levels of the sediment core were 2,218 and 85 µg/g, dry weight, respectively. Surface and deep (4.5 meter) sediment samples taken from Lake Kochejavr, which is located 120 kilometers from the Pechenganickel smelter, showed little difference in nickel concentrations (21 and 16 µg/g, dry weight, respectively), even though this lake does receive airborne emissions from the Pechenganickel plant (Kashulin et al. 2001). Nickel carried into creeks and streams from drainage and runoff originating from active or abandoned mining operations in the Black Hills of South Dakota can lead to increased concentrations of this metal in sediments (May et al. 2001). Nickel concentrations varied between 10 and 64 µg/g, dry weight, depending on proximity to nearby mines.

Nickel occurs naturally in the earth's crust with an average concentration of 0.0086% (86 ppm) (Duke 1980a). The nickel content of soil may vary depending on local geology. A nickel content of 0.5% (5,000 ppm) is common in podzol soil in southeastern United States, and nickel concentrations of >1,000 ppm are not unusual in glacial till in southern Quebec. Both areas are underlain with ultramafic rock, which is rich in nickel. Typical nickel levels reported in soil range from 4 to 80 ppm. In a region north of Sydney, Australia, nickel concentrations as high as 2,030 ppm have been reported in ferrosol topsoils, which are naturally-enriched in nickel throughout the weathering of underlying haematite, magnetite, quartz, and kaolinite minerals (Lottermoser 2002). A soil survey by the U.S. Geological Survey throughout the United States reported that nickel concentrations ranged from <5 to 700 ppm, with a geometric mean of 13 ± 2.31 ppm, ranking 15th among the 50 elements surveyed (Shacklette and

6. POTENTIAL FOR HUMAN EXPOSURE

Boerngen 1984). In this survey, samples were taken at 20 cm from 1,318 sampling sites. Cultivated soils contained 5–500 ppm of nickel, with a typical concentration of 50 ppm (Bennett 1984). Nickel concentrations in Canadian soils were generally 5–50 ppm (Webber and Shames 1987). An extensive survey in England and Wales reported that nickel concentrations typically ranged from 4 to 80 ppm, with a median value of 26 ppm (Bennett 1984). The average farm soil in the United States contained >30 ppm nickel (NAS 1975). Mean nickel concentrations in the forest floor from samples collected from 78 sites in nine northeastern states averaged 11 ± 0.8 ppm (Friedland et al. 1986).

Nickel concentrations in contaminated soils within ≈ 8 km of the large nickel smelter at Sudbury, Ontario, ranged from 80 to 5,100 ppm (Duke 1980b). A study of wetland soil-sediment in Sudbury found 9,372 and 5,518 ppm of nickel at sites located 2.0 and 3.1 km from the smelter, respectively (Taylor and Crowder 1983). Nickel concentrations declined logarithmically with increasing distance from the smelter. This indicates that nickel accumulations result from atmospheric deposition and soil runoff (Taylor and Crowder 1983). In a more recent survey of nickel content in soils in the Sudbury region, soil samples were taken within 5 km of each of the three smelters located in the area, Copper Cliff, Coniston, and Falconbridge (Adamo et al. 1996). Mean total concentrations of nickel in soil (based on dry weight) of 580, 286, and 210 mg/kg were obtained for the three sites, respectively. Concentration ranges were 80–2149, 156–628, and 23–475 mg/kg for the Copper Cliff, Coniston and Falconbridge sites, respectively.

Soils from the Idaho National Engineering Laboratory (INEL) and two background sites in southern Idaho had geometric mean nickel concentrations of 11.8–23.4 ppm dry weight; concentrations are significantly higher near INEL (Rope et al. 1988). The coal-fired steam plant that was constructed at the laboratory in 1982–1983 may be responsible for the higher nickel concentrations.

Nickel concentrations in 57 sludge-treated soils in an agricultural area of Ontario, Canada, ranged from 6.2 to 34 ppm (dry weight), with a mean of 20 ppm (Webber and Shames 1987). For 252 untreated soils, the range and mean values were 4.0–48 and 16.2 ppm, respectively. The mean for sludge-treated soil was significantly elevated.

6.4.4 Other Environmental Media

There have been several studies regarding nickel content in an average diet. Current information on the dietary intake of nickel in the United States is based on data gathered from the NHEXAS study. Nickel

6. POTENTIAL FOR HUMAN EXPOSURE

concentrations were measured in duplicate diet samples which, in combination with study participant's estimates of food and water intake, were used to determine both the overall concentration of nickel in combined solids and liquids in the total diet and the average nickel intake of study participants. In the EPA Region 5 (Illinois, Indiana, Michigan, Minnesota, Ohio, and Wisconsin) study, the mean and median concentrations of nickel in combined dietary solids and liquids were 47 and 43 $\mu\text{g}/\text{kg}$, respectively (Thomas et al. 1999).

In other studies of nickel in the diet, Myron et al. (1978) analyzed nine institutional diets consisting of three meals each. Four of these meals were sampled from the student center at the University of North Dakota. The remaining five diets were special diets from a rehabilitation hospital. The average nickel concentration and nickel content of the student meals ranged from 0.19 to 0.29 ppm and from 140 to 221 μg , respectively. For the hospital meals, the nickel concentration ranged from 0.21 ppm (107 μg) in the puree meals to 0.41 ppm (176 μg) in the low-calorie meal. Breakfast had the lowest nickel content. The average daily dietary nickel intake for the nine diets was 168 ± 11 μg . The average nickel concentration in the food was 0.27 ppm (dry weight). These results are comparable with estimated daily intakes of nickel of 150 μg in Denmark, 73–142 μg in Switzerland, and 140–150 μg in the United Kingdom (IARC 1990; Nielsen and Flyvholm 1984). A 1962 study that used the nickel content of individual foods to estimate average dietary nickel intake reported intakes of 300–600 μg , which are much higher than those reported above (Grandjean 1984).

A study of dietary intake of heavy metals for 44 individuals (21 men, 43 women) living in central Italy was conducted using dietary history, weighted record methods, and concurrent chemical analysis of duplicate portions (Alberti-Fidanza et al. 2003). Based on chemical analysis, the mean (± 1 SD) daily intakes of nickel were measured to be 222.3 ± 87.7 μg in men and 165.7 ± 53.8 μg in women. Calculation of daily nickel intake based on dietary history or food basket data resulted in lower intake values for both men and women. Based on dietary histories, daily nickel intakes for men and women were determined to be 105.3 ± 32.6 and 84.8 ± 24.9 μg , respectively; calculations based on food basket data gave daily nickel intakes of 123.8 ± 37.8 and 98.3 ± 25.6 μg for men and women, respectively. In another study of trace metal intake from components in the Italian diet, it was determined that the average Italian adult obtained 280 μg of nickel per week through the consumption of beverages such as wine, beer, coffee, tea, and mineral water (Minoia et al. 1994). Wine and tea were identified as the largest sources of nickel intake at 25.2 and 15.6 $\mu\text{g}/\text{week}$, respectively.

6. POTENTIAL FOR HUMAN EXPOSURE

The nickel content of specific food items has also been determined. In the average Danish diet, the ranges of mean nickel levels in various food categories (in ppm) have been reported as follows: milk products, 0.01–0.1; meat, fish, and eggs, 0.02–0.11; vegetables, 0.04–0.52; fruits, 0.01–0.31; and grains, 0.1–1.76 (IARC 1990; Nielsen and Flyvholm 1984). The mean nickel level in meats, fruits, and vegetables is ≤ 0.2 ppm. The foods with the highest mean nickel content were oatmeal, spinach, asparagus, and peas. Nuts and cocoa may have nickel levels as high as 3 and 10 ppm, respectively (IARC 1990). In a market basket survey completed in the United States (Pennington and Jones 1987), the highest average levels of nickel in $\mu\text{g}/100\text{ g}$ were found in nuts (128.2), legumes (55), sweeteners (31.6), grains and grain products (26.2), and mixed dishes and soups (25.3). From data gathered in the FDA Total Diet Study 1991–1996, the mean and median nickel concentrations in the food items that were surveyed were 0.136 and 0.057 mg/kg, respectively (Capar and Cunningham 2000). The highest concentrations of nickel were found in mixed nuts (3.04 mg/kg), oat ring cereal (2.32 mg/kg), chocolate syrup (1.04 mg/kg), granola cereal (1.01 mg/kg), and peanuts (0.956 mg/kg). Other products with notable nickel concentrations are legumes and nuts (0.368–3.04 mg/kg), cereals containing largely whole wheat, corn, oats, or rice (0.216–2.32 mg/kg), chocolate products (0.19–1.04 mg/kg), and canned peaches and pineapple juice (0.408–0.668 mg/kg). In an analysis of trace metals in tissue samples taken from livestock and poultry, mean nickel concentrations were 0.23–0.82 ppm in muscle, 0.23–0.29 ppm in liver, and 0.28–0.57 ppm in kidney (Coleman et al. 1992).

A Canadian survey of nickel in infant formulas gave a median value of 3.53 $\mu\text{g}/\text{L}$ for evaporated milk (Dabeka 1989). Different types of milk-based formulas contained from 5.8 to 28.9 μg nickel/L (Dabeka 1989). All concentrations are on a ready-to-use basis. Formulas fortified with iron had a higher nickel content. The median nickel content of soy-based formula ranged from 31.2 to 187 μg nickel/L. The average daily dietary intake of nickel by infants between the ages of 0 and 12 months could vary from 35.7 μg (4.5 $\mu\text{g}/\text{kg}$) (if evaporated milk was fed) to 74.7 μg (10.2 $\mu\text{g}/\text{kg}$) (if concentrated liquid soy-based formula was used). Infant formula (base not stated) in the United States contained an average of 0.2 μg nickel/100 g (Pennington and Jones 1987).

There is limited evidence that stainless steel pots and utensils may release nickel into acid solution (IARC 1990). Six stainless steel pots of different origins were tested to see whether they would release nickel by boiling 350 mL of 5% acetic acid in them for 5 minutes (Kuligowski and Halperin 1992). The resulting concentrations of nickel ranged from 0.01 to 0.21 ppm. Cooking acidic fruits in new stainless steel pans resulted in an increase of nickel that was about one-fifth the average daily nickel intake (Flint and Packirisamy 1995). Further use of the pans did not result in any release of nickel into the food. The use

6. POTENTIAL FOR HUMAN EXPOSURE

of nickel-containing catalysts in the hydrogenation of food fats may contribute to elevated nickel levels in food (Mastromatteo 1986). Grain milling may also lead to higher nickel levels (IARC 1990). The results from a recent study that attempted to identify the influence of the container on the trace metal content of preserved pork products showed no clear evidence that the metal container contributed to the metal content of the food (Brito et al. 1990). The nickel concentration was highest in products in china and glass containers, rather than those in metal and plastic containers.

The nickel content of cigarettes is 1–3 µg; ~10–20% of this nickel is released in mainstream smoke (Sunderman 1986). This indicates that 2–12 µg of nickel are inhaled for each pack of cigarettes smoked. Most of the nickel is in the gaseous phase, but the chemical form of the nickel is unknown (IARC 1990).

In a comprehensive survey of heavy metals in sewage sludge, 31 sludges from 23 American cities were analyzed by electrothermal atomic absorption spectroscopy (AAS) (Mumma et al. 1984). The nickel concentration in the sludges ranged from 29.0 to 800 ppm (dry weight) and had a median value of 195 ppm. The highest concentration of nickel in sludge was in Detroit, Michigan. For comparison, the concentration of nickel in cow manure was 28.0 ppm. In another study of heavy metal in sludges generated at waste water treatment plants in 16 large U.S. cities, nickel concentrations (dry weight) were found to range from 18 to 186 ppm, with a median value of 66.8 ppm (Gutemann et al. 1994).

Nickel was detected in a large number of the 283 point samples taken from leachate collected from 48 codisposal, hazardous, or municipal solid waste (MSW) sites (Gibbons et al. 1999). Codisposal sites were defined as those facilities accepting municipal wastes and relatively large volumes of industrial sludges, liquids, and solids. Dissolved nickel was detected in 43 of 45 codisposal sites, all 48 old (accepting waste before 1986) hazardous waste sites, all 29 old (accepting waste before 1984) MSW sites, and 1 of 1 new (accepting waste after 1984) MSW site. Solid nickel was detected in 105 of 111 codisposal sites, 108 of 126 old (accepting waste before 1986) hazardous waste sites, 108 of 116 old (accepting waste before 1984) MSW sites, and 36 of 43 new (accepting waste after 1984) MSW sites.

6.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Nickel occurs naturally in the earth's crust, and the general population will be exposed to low levels of nickel in ambient air, water, and food. The average daily dietary intake of nickel in food ranges between 69 and 162 µg/day (O'Rourke et al. 1999; Pennington and Jones 1987; Thomas et al. 1999). The daily intake from drinking water is ~8 µg, assuming a median nickel concentration of ~4 µg/L and a

6. POTENTIAL FOR HUMAN EXPOSURE

consumption rate of 2 L water/day. For the highest municipal level in drinking water, which is 68 µg/L in Sudbury, Ontario, the average daily intake of nickel would be 140 µg. Assuming that a person inhales 20 m³ air/day and the range of average nickel concentrations in ambient air in the United States is 2.22 ng/m³, the average nickel intake by inhalation would be 0.0444 µg/day. Based on the highest ambient nickel levels reported for the Copper Cliff (6,100 ng/m³) and Sudbury basin region (732 ng/m³) in Ontario (CEPA 1994), the daily inhalation intake for individual living in these areas could have been as high as 122 and 15 µg/day, respectively. However, based on the mean ambient nickel concentrations measured in Sudbury area of 21 ng/m³ (CEPA 1994) the daily nickel the average daily nickel intake is estimated to be 0.42 µg/day. The nickel intake via inhalation is, therefore, a minor source of nickel to the general, nonsmoking population.

A market basket survey in England completed in 1984 estimated a dietary intake of 154–166 µg/day or 2.2–2.4 µg/kg/day for a 70-kg person (Smart and Sherlock 1987). Dietary intake of nickel in the United States has been estimated to range from 69 µg/day for 6–11-month-old infants to 162 µg/day for teenage boys, with a level of 146.2 µg/day or 2 µg/kg/day for a 25–30-year-old male weighing 70 kg (Pennington and Jones 1987). More recent data on nickel intakes from the U.S. diet come from the results of the NHEXAS studies. Mean and median dietary intakes of nickel for study participants in the EPA Region 5 study were calculated to be 2.2 and 1.4 µg/kg body weight/day, respectively, or 154 and 98 µg/day for a 70-kg adult, respectively (Thomas et al. 1999). O'Rourke et al. (1999) have taken the dietary nickel data obtained from the Arizona study and determined the dietary nickel intake for various subpopulations (Table 6-4). The mean daily nickel intake for all subjects was 153 µg/day, with the highest mean intake for an adult male (163 µg/day) and lowest intake for children (125 µg/day). Hispanic study participants were found to have a lower mean dietary intake (141 µg/day) than non-Hispanic participants (155 µg/day). Total nickel intake for Canadians in the general population has been estimated to range from 4.4 to 22.1 µg/kg/day, with greater intake estimated for infants than for adults (CEPA 1994). Food, from which nickel is poorly absorbed, accounted for most of the intake (4.4–22 µg/kg/day). It was estimated that cigarette smoking may increase total daily intake by 0.12–0.15 µg/kg/day. Living in the vicinity of Sudbury, Ontario, where large nickel deposits are found, water intake of nickel for individuals aged 12 years old or older ranged from 0.6–2.5 µg/kg/day. However, the estimated water intake of nickel increased with decreasing age of the study group, for example 0.87–3.6 µg/kg/day for children ages 5–11 years old to 2.8–12 µg/kg/day for newborns and infants under the age of 0.5 years.

In another approach to determining daily nickel intake within subpopulations in the United States, Moschandreas et al. (2002) used the Dietary Exposure Potential Model (DEPM) and data obtained from

6. POTENTIAL FOR HUMAN EXPOSURE

Table 6-4. Total Dietary Exposure Estimates of Study Participants to Nickel Based on the Dietary Information Obtained from the NHEXAS Arizona Study^a

Exposure population	Number of participants evaluated	Daily nickel intake (µg)		
		Mean intake	Median intake	Range
All subjects	176	153	135	27–562
Adult male (>18 years of age)	55	163	145	38–372
Adult female (>18 years of age)	86	157	135	23–563
Children (<18 years of age) ^b	35	125	107	31–343
Hispanic	54	141	134	27–401
Non-Hispanic	119	155	132	42–563

^a O'Rourke et al. 1999^b Either gender

6. POTENTIAL FOR HUMAN EXPOSURE

Combined National Residue Database (CNRD) to estimate dietary nickel intake based on food consumption patterns in subpopulations and nickel content in specific food items. The food items used in the model are based on 11 food groups consisting of approximately 800 exposure core foods that represent 6,500 common food items. The results of their model (Table 6-5) yielded an average dietary nickel intake in the U.S. population of 0.374 $\mu\text{g}/\text{kg}$ body weight/day, or 26.2 $\mu\text{g}/\text{day}$ for a 70-kg adult. Their results also indicate that children under the age of 7 have a nickel intake that is at least 1.8 times higher than the average for the overall population. However, the estimates obtained for dietary nickel intake from the DEPM model are lower than the daily nickel intakes determined from the NHEXAS study (Table 6-4). Moschandreas et al. attribute these differences in intake values for nickel to differences in study populations, methods for assigning values to measurements that are below the level of detection, and potential errors in recording portion sizes in the NHEXAS study.

The general population is also exposed to nickel in nickel alloys and nickel-plated materials including steel, coins, and jewelry (Barceloux 1999). Jewelry and other items made of silver may either contain, or be coated with, nickel to reduce oxidation. White gold contains 10–15% nickel and some gold-plated items may have a nickel undercoating. Residual nickel may be present in soaps, fats, and oils hydrogenated with nickel catalysts (Sunderman 1986).

A NOES survey conducted by NIOSH from 1981 to 1983 estimated that 727,240 workers are potentially exposed to nickel metal, alloys, dust, fumes, salts, or inorganic nickel compounds in the United States (NIOSH 1990). Seventy percent of these estimated exposures are to nickel of an unknown molecular formula. The numbers of workers estimated to be exposed to nickel chloride, nickel oxide, and nickel sulfate are 48,717, 18,166, and 56,844, respectively. The estimate is provisional because all of the data for trade name products that may contain nickel have not been analyzed. The NOES was based on field surveys of 4,490 businesses employing nearly 1.8 million workers and was designed as a nationwide survey based on a statistical sample of virtually all workplace environments in the United States where eight or more persons are employed in all standard industrial codes except mining or agriculture. Industries with especially large numbers of potentially exposed workers include the following: plumbing, heating, air conditioning, pressed and blown glass, steel, plating and polishing, aircraft, shipbuilding, railroad, control and measuring instruments, and repair services (NIOSH 1990).

Occupational exposure to nickel will be highest for those involved in production, processing, and use of nickel. There are currently no people in the United States employed in nickel mines, smelters, and refineries at the end of 2001. Primary nickel production in the United States ceased for several years in

6. POTENTIAL FOR HUMAN EXPOSURE

Table 6-5. Dietary Exposure Estimates of U.S. Populations to Nickel Based on the Dietary Exposure Potential Model (DEPM)^a

Subpopulation	Nickel intake (µg/kg BW ^b /day)
U.S. population	0.374
Age/gender	
Nonnursing infants	0.870 ^c
Children 1–6	0.669
Children 7–12	0.425
Females 13–19	0.281
Females 20+	0.350
Females 55+	0.368
Males 13–19	0.324
Males 20+	0.342
Males 55+	0.369
Ethnicity	
Hispanic	0.407
Non-Hispanic white	0.424 ^c
Non-Hispanic black	0.295
Non-Hispanic other	0.258
Geographic region ^d	
North central	0.238
Northeast	0.379
Southern	0.359
Western	0.423 ^c
Family income ^e	
Poverty 0–130%	0.420 ^c
Poverty 131%+	0.362

^a Moschandreas et al. 2002^b BW = body weight^c Values indicate the maximum exposure to nickel for each subpopulation group.^d The regional classification is as defined by the U.S. Department of Agriculture, and is based upon U.S. Census Bureau regions.^e Annual household income as a percentage of the Poverty Index.

6. POTENTIAL FOR HUMAN EXPOSURE

the late 1980s (Kirk 1988a). The mining and smelting operation in Riddle, Oregon, was reactivated in 1989–1990, and was decommissioned in 2001 (Kuck 2001). The concentration range of airborne nickel that workers were exposed to in laterite mining and smelting in Riddle, Oregon, was 4–420 $\mu\text{g}/\text{m}^3$ (Warner 1984). The ranges of airborne nickel concentrations reported for other industries are as follows: stainless steel production, <1–189 $\mu\text{g}/\text{m}^3$; high nickel alloy production, 1–4.4 $\mu\text{g}/\text{m}^3$; foundry operations, from not detectable to 900 $\mu\text{g}/\text{m}^3$; electroplating, from <2 to <16 $\mu\text{g}/\text{m}^3$; nickel-cadmium battery manufacture, 20–1,910 $\mu\text{g}/\text{m}^3$; nickel catalyst production from nickel sulfate, 1–1,240 $\mu\text{g}/\text{m}^3$; production of nickel salts from nickel or nickel oxide, 9–590 $\mu\text{g}/\text{m}^3$; and production of wrought nickel and alloys from metal powder, 1–60,000 $\mu\text{g}/\text{m}^3$ (Anttila et al. 1998; Haber et al. 2000; Magari et al. 2002; Warner 1984). Average nickel concentrations for selected work areas or operations in these industries, other than producing wrought nickel and alloys from metal powder, range from <3 to 378 $\mu\text{g}/\text{m}^3$; for wrought nickel and alloy production from metal powder, the average concentration is 1,500 $\mu\text{g}/\text{m}^3$. Operations that produce the highest levels of airborne nickel are those that involve grinding, welding, and handling powders. Not only do occupational exposures vary widely among these operations and industries, but also the form of nickel that workers are exposed to varies (Table 6-6). Because sulfur has a deleterious effect on many metals and alloys, nickel sulfate and sulfidic nickel compounds are generally not found in metallurgical workplaces (Warner 1984). Nickel subsulfide is known to exist in only one application in nickel-using industries, namely in certain spent catalysts. Nickel oxide is used as a raw material in steel production, and oxide fumes and dust may occur in melting, casting, and welding operations. There are probably more exposures to metallic nickel in nickel-using industries than in nickel-producing industries. These occur during powder handling, grinding, and polishing operations and in casting operations.

Nickel is an essential trace element for animals (Sunderman 1986), and a 70-kg reference man contains 10 mg of nickel, giving an average body concentration of 0.1 ppm (Iyengar 1986). The highest tissue concentrations of nickel are found in the lungs of nickel smelting and refinery workers. The highest nickel concentration reported in lung tissue of 39 nickel refinery workers autopsied in 1978–1984 was 1,344 ppm (dry weight), compared to 1.7 ppm in unexposed persons (Andersen and Svenes 1989). In another study of nickel content in the lungs of 15 former nickel refinery workers, the arithmetic mean (± 1 SD) for nickel concentrations in workers was 50 ± 150 $\mu\text{g}/\text{g}$, dry weight, in comparison to a value of 0.74 ± 0.44 $\mu\text{g}/\text{g}$ in 10 individuals not connected to the refinery industry (Svenes and Anderson 1998).

Ten studies of nickel in human milk gave disparate results. Six median values ranged from 5 to 16 $\mu\text{g}/\text{L}$, and 10 mean values ranged from 1.5 to 39 $\mu\text{g}/\text{L}$ (Iyengar 1989). Five of the six medians ranged from

6. POTENTIAL FOR HUMAN EXPOSURE

Table 6-6. Nickel Levels in Air and Distribution of Different Forms of Nickel as a Proportion (by Weight) of Total Nickel in Selected Departments and Time Periods at a Nickel Refinery in Norway^a

Department and period	Total nickel in air (mg/m ³)	Proportion of total nickel			
		Soluble nickel	Sulfidic nickel	Metallic nickel	Oxidic nickel
Crushing and grinding					
1990–1994	0.7–1.4	0.12	0.72	0.11	0.04
Smelter					
1910–1929	4.0	0.10	0.05	0.01	0.84
1930–1950	4.0	0.10	0.05	0.08	0.77
1951–1977	2.6–4.4	0.10	0.04	0.18	0.68
Calcining, smelting					
1951–1977	1.5–3.4	0.10	0.05	0.01	0.84
1978–1994	0.5	0.12	0.13	0.01	0.74
Roasting					
1910–1977	1.9–5.3	0.10	0.15	0.03	0.72
1978–1994	0.4	0.15	0.05	0.00	0.80
Copper leaching					
1910–1994	0.1–1.5	0.49	0.01	0.01	0.49
Copper electrolysis					
1910–1994	0.03–0.2	0.80	0.04	0.04	0.13
Copper cementation					
1927–1977	0.6–1.2	0.45	0.05	0.45	0.05
Electrolytic purification					
1927–1977	0.2–0.5	0.80	0.03	0.15	0.02
1978–1994	0.03–0.2	0.98	0.01	0.00	0.01
Nickel electrolysis					
1910–1977	0.1–0.2	0.87	0.05	0.01	0.08
1978–1994	0.03–0.1	0.83	0.04	0.02	0.11

^aGrimsrud et al. 2002

6. POTENTIAL FOR HUMAN EXPOSURE

11 to 16 µg/L. The lowest and highest mean values were from Finland and Germany GDR, respectively. None of the studies were from the United States. Individual values ranged from not detectable to 130 µg nickel/L.

Nickel concentrations in human serum taken from 30 individuals not occupationally exposed to nickel ranged from <0.05 to 1.05 µg/L with a mean value of 0.34 µg/L (Barceloux 1999). In another example, nickel concentrations in serum obtained from individuals without occupational exposures to nickel ranged from 0.18 to 0.54 µg/L with an average of 0.36 µg/L (Christensen 1995). Serum nickel levels in hospital workers averaged 0.6 ± 0.3 µg/L in Sudbury, Ontario, versus 0.2 ± 0.2 µg/L in Hartford, Connecticut (Hopfer et al. 1989). Measurements of nickel content of tap water in these communities were reported as 109 ± 46 and 0.4 ± 0.2 µg/L, respectively (Hopfer et al. 1989). A mean nickel concentration of 4.80 ± 2.69 µg/L was measured in urine samples collected for the NHEXAS Arizona study (EPA 2003t). Concentrations of nickel in the blood and urine of workers at a rolling mill in Poland were 18.5 ± 4.0 and 25.7 ± 5.1 µg/L, respectively (Baranowska-Dutkiewicz et al. 1992). Mean concentrations of nickel in urine of individuals not occupationally exposed to nickel are generally <2 µg/L and can range as high as 9–10 µg/L (95% upper confidence limit) in healthy adults (Barceloux 1999). Workers at a galvanizing plant in Brazil exposed to airborne nickel sulfate at concentrations of 2.8–116.7 µg/m³ had nickel concentrations in their urine ranging between 2.1 and 58.7 µg/g creatinine (2.3–54.9 µg Ni/L) with mean values of 8.7 ± 7.8 and 14.7 ± 13.5 µg/g creatinine (10.5 ± 7.5 and 20.6 ± 18.1 µg Ni/L) in preshift and postshift samples, respectively (Oliveira et al. 2000). Mean concentrations of nickel in the urine of the control group (workers in a zinc plating plant) were 3.7 ± 2.5 µg/g creatinine or 4.9 ± 2.2 µg/L. Nickel concentrations in the urine of preschool children in Poland were 10.6 ± 4.1 and 9.4 ± 4.7 µg/L for children from an industrial region and a health resort, respectively (Baranowska-Dutkiewicz et al. 1992). After reviewing studies of nickel concentrations in humans, Templeton et al. (1994) indicated that the most reliable reference values were 0.2 µg/L for nickel in serum of healthy adults and 1–3 µg/L for nickel in urine. These values are dependent on food and fluid intake and environmental factors. Fewer studies of nickel in whole blood were identified, and a reference value was not suggested.

Fingernail samples from 71 Americans contained 0.57 ppm of nickel; samples from residents of Japan, India, Canada, and Poland had nickel concentrations that ranged from 1.1 to 3.9 ppm (Takagi et al. 1988). Nickel levels are higher in males than in females. Higher levels occur in younger people and decrease with age. The mean concentration of nickel in hair samples from 55 men and women from Scranton, Pennsylvania, was 1.01 ppm; populations from cities in Japan, India, Canada, and Poland had mean nickel levels between 0.26 and 2.70 ppm (Takagi et al. 1986). A more recent National Health and

6. POTENTIAL FOR HUMAN EXPOSURE

Nutritional Examination Survey II of hair from a random sample of 271 adults, ages 20–71, from three communities had geometric mean and median nickel levels of 0.39 and 0.45 ppm, respectively. Ten percent of the group had nickel levels >1.50 ppm (DiPietro et al. 1989).

The nickel content of most natural vegetation is 0.05–5 ppm on a dry weight basis (NAS 1975). Near source areas, nickel on plants may be elevated because of direct foliar deposition. Some species of plants have the ability to hyperaccumulate nickel (Brooks 1980). The concentration in the leaves of *Alyssum bertolonii* contained 120 ppm nickel. These plants are thought to produce organic ligands that complex with nickel.

The modal concentration of nickel in 159 species of edible fin fish from the U.S. National Marine Fisheries Survey was 0.2–0.3 ppm (wet weight) (Heit et al. 1989). Jenkins (1980) has compiled literature concentrations of nickel levels in aquatic species. The ranges of nickel concentrations in freshwater fish, marine fish, and mollusks from areas thought to be uncontaminated are from <0.2 to 2.0, from not detectable to 4.0, and from 0.4 to 2.0 ppm (wet weight), respectively. The highest levels found near sources of pollution, especially near nickel smelters, were 51.6 ppm for freshwater fish and 191.0 ppm for mollusks. The nickel content of muscle tissue of several fish species collected from metal-contaminated lakes near Sudbury, Ontario, was below the detection limit (2.0 ppm dry weight), except for two of four yellow perch, which had levels of 2.8 and 3.4 ppm (Bradley and Morris 1986). A more recent survey of metals in stocked lake trout in five lakes near Sudbury, Ontario, reported that concentrations of metal in trout muscle were not significantly different from those in the hatchery (0.34–0.83 ppm wet weight versus 0.49 ppm) (Bowlby et al. 1988). Nickel concentrations in the lower Savannah River and Savannah National Wildlife Refuge in Georgia were higher than those reported above for uncontaminated areas. These levels were consistently higher in gar (2.35–6.67 ppm wet weight) than in catfish (0.37–1.41 ppm) (Winger et al. 1990). Nickel could not be measured above the detection limit (0.5 µg/g, dry weight) in livers taken from lesser scaup collected along the Mississippi Flyway between Manitoba and Louisiana (Custer et al. 2003). As part of the National Status and Trends Program for Marine Environmental Quality, the concentration of nickel in oysters and mussels was investigated (NOAA 1987). The nickel concentration in bivalve tissue collected in 1986 ranged from 0.55 to 12.57 ppm (dry weight). The highest tissue concentration was found in Matagorda Bay, Texas, and the second highest concentration, 6.57 ppm, was found in both Tomales Bay, California, and Chesapeake Bay, Maryland. Oysters around three coastal marinas in South Carolina with sediment nickel levels of 25.8–40.8 ppm (dry weight) had levels of 0.3–5.2 ppm (Marcus and Thompson 1986). Mean nickel levels in oysters at four sites in the Mississippi Sound varied from <0.5 to 4.7 ppm (wet weight) (Lytle and Lytle 1990).

6. POTENTIAL FOR HUMAN EXPOSURE

6.6 EXPOSURES OF CHILDREN

This section focuses on exposures from conception to maturity at 18 years in humans. Differences from adults in susceptibility to hazardous substances are discussed in 3.7 Children's Susceptibility.

Children are not small adults. A child's exposure may differ from an adult's exposure in many ways. Children drink more fluids, eat more food, breathe more air per kilogram of body weight, and have a larger skin surface in proportion to their body volume. A child's diet often differs from that of adults. The developing human's source of nutrition changes with age: from placental nourishment to breast milk or formula to the diet of older children who eat more of certain types of foods than adults. A child's behavior and lifestyle also influence exposure. Children crawl on the floor, put things in their mouths, sometimes eat inappropriate things (such as dirt or paint chips), and spend more time outdoors. Children also are closer to the ground, and they do not use the judgment of adults to avoid hazards (NRC 1993).

Exposures of children to airborne nickel are expected to be similar to those found for adults. However, differences in the exposure to nickel contained in deposited particulates (e.g., household dust) are expected to be higher in children, due to greater contact of children with floors and other surfaces, in addition to greater oral and dermal contact with these deposited particulates through the mouthing of toys, hands, feet, etc. Concentrations of nickel in dust collected from homes in Ottawa, Ontario, averaged 62.9 mg/kg with values as high as 116.4 mg/kg (Butte and Heinzow 2002). However, it is not known how much nickel a child absorbs through oral or dermal contact with household dust.

Nickel that is dissolved in water is expected to be a minor exposure route for children, due to the generally low concentrations of nickel in drinking water and groundwater (Sections 6.4.2 and 6.5). However, in areas near nickel smelters and refineries where source water used to produce drinking water is contaminated with nickel, intake of nickel through drinking water for individuals in the affected area will be elevated above that for individuals in the surrounding region whose drinking water is unaffected by these sources of nickel contamination, but is expected to be less than nickel intake through food. Exposure to nickel through consumption of human breast milk is expected to be comparable to milk-based and soy-based formulas, based on the similar concentration ranges of nickel in these fluids (Dabeka 1989; FDA 2000; Iyengar 1989).

6. POTENTIAL FOR HUMAN EXPOSURE

Another source of nickel exposure in children is through soil. Children generally receive higher exposure to soil contaminants per unit body weight than adults (Lottermoser 2002). Small children have large surface-to-mass ratios, which provide a greater potential to transdermally absorbed compounds, especially for children crawling in dirt. Also, the skin of newborns and children is more permeable than adult skin. Nickel in an ionized form, such as nickel salts, does not penetrate intact skin but can be absorbed at sites of injury to skin or in conjunction with nickel-induced contact dermatitis (Barceloux 1999). However, nickel exposure through dermal exposure is minimal compared to exposures to nickel through ingestion of soil. The largest target population at greatest risk are children between the ages of 2 and 3 years old as a result of hand-to-mouth activities and those with soil-eating disorders (Lottermoser 2002). A child's intake of nickel through ingestion of soil could be especially important in areas where soils that are naturally enriched with nickel (for example, some soils in the southeastern United States, southern Ontario, or eastern Australia) or have been contaminated with nickel (for example in the Sudbury, Ontario, region) (Section 6.4.3). However, due to the limited bioavailability of nickel in some soils, the amount of nickel that a child actually absorbs from ingested soils could be rather limited. For example, ingestion of 100 mg of ferrosol soil containing 149 mg nickel per kg of soil is calculated to contribute an intake of 0.000149 mg nickel/day, assuming a relative bioavailability for nickel of 1% (Lottermoser 2002).

The primary route of nickel exposure in children is expected to be through the diet. Measurements of nickel in duplicate diet samples obtained from the EPA Region 5 studies indicates that average nickel concentration in combined solids and liquids of 47 µg/kg, which is higher than the average nickel concentration in drinking water of approximately 5 µg/kg (5.3 µg/L) (Thomas et al. 1999). Using the portion size information recorded by study participants in the NHEXAS Arizona study, daily dietary intakes of nickel for children (<18 years of age) have been calculated to range from 31 to 343 µg, with a mean value of 125 µg (O'Rourke et al. 1999). These intake levels were lower than the average dietary nickel intake of 153 µg/day calculated for the overall study population (Table 6-4). Information on dietary nickel intake for non-nursing children and children ages 1–6 (Table 6-5) obtained from DEPM model (Moschandreas et al. 2002) indicates that these children have a higher intake of nickel than the average intake for the U.S. population. Even so, the daily intake of nickel in these children is estimated (4–13 µg/day based on 6–20 kg total body weight) to be much lower than the average dietary nickel intake (125 µg/day) obtained from the NHEXAS study. Also, results from a study of dietary nickel in 2-year-old children in the United Kingdom, where an average daily intake of 81 µg/day (range of

6. POTENTIAL FOR HUMAN EXPOSURE

14–260 µg/day) was estimated from the weekly nickel intake of 0.57 mg of nickel (range of 0.1–1.8 mg) given in the reference (Smart et al. 1987), would suggest a higher daily nickel intake in young children than is indicated based on the results of the DEPM model.

6.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

In discussing nickel exposure, it is important to consider what form of nickel a person is exposed to and its bioavailability. Such information is not often available. Although high concentrations of nickel may be found in contaminated soil and sediment, it may be embedded in a crystalline matrix or bound to hydrated iron, aluminum, and manganese oxides and, therefore, not bioavailable.

Nickel-containing alloys are used in patients in joint prostheses, sutures, clips, and screws for fractured bones. Corrosion of these implants may lead to elevated nickel levels in the surrounding tissue and to the release of nickel into extracellular fluid (IARC 1990; Ries et al. 2003; Sunderman 1989a; Sunderman et al. 1986, 1989c). Serum albumin solutions used for intravenous infusion fluids have been reported to contain as much as 222 µg nickel/L. Dialysis fluid has been reported to contain as much as 0.82 µg nickel/L. Patients receiving transfusions may be exposed to high levels of nickel.

People who live near or work at facilities that produce stainless steel and other nickel-containing alloys, oil-fired power plants, coal-fired power plants, and refuse incinerators may be exposed to high levels of nickel in airborne dust, soil, and vegetation. People who live near or work at waste sites that receive waste from nickel-producing or using industries or that handle bottom ash or fly ash from power plants or refuse incinerators may also be exposed to higher levels of nickel (Newhook et al. 2003). Exposure would result from inhalation, dermal contact, or ingestion of contaminated soil or vegetation. It is possible that nickel from waste sites will contaminate groundwater. This situation is most probable with electroplating waste. People using this groundwater may be exposed to high nickel concentrations.

6.8 ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of nickel is available. Where adequate information is not available, ATSDR, in conjunction with the National Toxicology Program (NTP), is required to assure the

6. POTENTIAL FOR HUMAN EXPOSURE

initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of nickel.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that if met would reduce the uncertainties of human health assessment. This definition should not be interpreted to mean that all data needs discussed in this section must be filled. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

6.8.1 Identification of Data Needs

Physical and Chemical Properties. Except for differences between black and green nickel oxide, the physical and chemical properties of nickel and its compounds reported in Table 4-2 (HSDB 2003) have been adequately characterized.

Production, Import/Export, Use, and Release and Disposal. Information on the production, import, export, and use of nickel metal, nickel alloys, and nickel compounds is readily available (Chamberlain 1985; Kirk 1988a, 1988b; Kuck 2001; NTD 1996; Tien and Howson 1981). Except for recycling of metal scrap, little information is available regarding the disposal of nickel and its compounds.

According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit substance release and off-site transfer information to the EPA. The Toxics Release Inventory (TRI), which contains this information for 2000 is available on a yearly basis and provides a list of industrial production facilities and emissions.

Releases according to the TRI database are reported in Tables 6-1 and 6-2 (TRI01 2003). The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list. Much of the nickel released to the environment is transferred off-site for disposal and probably landfilled. Nickel wastes from former mining and smelting operations may have been discarded in large tailing piles. Acid conditions are often created in tailing piles from sulfidic ores that increase the potential for leaching (Wood 1987). This is not the case with lateritic deposits such as those found in Riddle, Oregon. Information regarding nickel leaching from slag heaps is important in assessing releases

6. POTENTIAL FOR HUMAN EXPOSURE

to the environment. More detailed information regarding disposal methods and the form of nickel disposed of is necessary to assess potential nickel exposure.

Environmental Fate. Nickel is an element and therefore, is not destroyed in the environment. In assessing human exposure, one must consider the form of nickel and its bioavailability. This information is site specific. Data regarding the forms of nickel in air, soil, and sediment are fragmentary and inadequate (Sadiq and Enfield 1984a; Schroeder et al. 1987). Also lacking is adequate information on the transformations that may occur, the transformation rates, and the conditions that facilitate these transformations. Information relating to the adsorption of nickel by soil and sediment is not adequate. In some situations, adsorption appears to be irreversible. In other situations, however, adsorption is reversible. More data would be helpful in detailing those situations where adsorbed nickel may be released and those where release is unlikely.

Bioavailability from Environmental Media. The absorption and distribution of nickel as a result of inhalation, ingestion, and dermal exposure are discussed in Sections 3.4.1 and 3.4.2. Quantitative data relating the physical/chemical properties of nickel (e.g., particle size, chemical forms of nickel) with its bioavailability are available for inhaled nickel. In aqueous media, nickel is in the form of the hexahydrate ion, which is poorly absorbed by most living organisms (Sunderman and Oskarsson 1991). Additional studies that examine the absorption of nickel from soil would be useful.

Food Chain Bioaccumulation. Data are available on the bioconcentration of nickel in fish and aquatic organisms (Birge and Black 1980; Callahan et al. 1978; McGeer et al. 2003; Suedel et al. 1994; Zarogian and Johnson 1984). Higher levels of nickel have been found in gar compared with catfish from the same environment (Winger et al. 1990). More data on different species of fish at different sites would be useful in explaining these results. Data are limited on the nickel levels in wild birds and mammals (Alberici et al. 1989; Dressler et al. 1986; Jenkins 1980). A larger database including information on both herbivorous and carnivorous species living in both polluted and unpolluted environments is desirable in establishing whether nickel biomagnification in the food chain occurs under some circumstances.

Exposure Levels in Environmental Media. Reliable monitoring data for the levels of nickel in contaminated media at hazardous waste sites are needed so that the information obtained on levels of nickel in the environment can be used in combination with the known body burden of nickel to assess the potential risk of adverse health effects in populations living in the vicinity of hazardous waste sites. Representative and recent monitoring data for nickel in air, water, and foods are essential for estimating

6. POTENTIAL FOR HUMAN EXPOSURE

the extent of exposure from each of these sources. Nickel levels in environmental media are often below the detection limit of the analytical method employed. When a substantial fraction of determinations of nickel levels in environmental samples are below the detection limit, an arithmetic mean may not adequately represent the data. Data on the levels of nickel in ambient air are available (Claiborne et al. 2002; EPA 1986a; Evans et al. 1984; Kinney et al. 2002; Koutrakis et al. 1992; Kowalczyk et al. 1982; Liroy et al. 1987; Salzman et al. 1985; Sweet et al. 1993; van Winkle and Scheff 2001; Vousta and Samara 2002; Wiersema et al. 1984). Data provided by EPA's National Human Exposure Assessment Study (NHEXAS) have contributed to the assessment of current levels of exposure to nickel by the U.S. population via inhalation, drinking water and food. Analyses of data obtained from the Arizona and EPA Region 5 NHEXAS studies (O'Rourke et al. 1999; Thomas et al. 1999) have provided information on daily dietary nickel intake for these study populations. These data have provided the first update of nickel content within the U.S. diet since the last comprehensive survey of nickel in U.S. drinking water in 1969–1970 (NAS 1975) and the information on dietary nickel that had been limited to one study from North Dakota (Myron et al. 1978). While these recent results are in agreement with ones from Europe (Alberti-Fidanza et al. 2003; IARC 1990), they do differ from the estimated dietary nickel intakes obtained by Moschandreas et al. (2002). Therefore, additional data on nickel content within the U.S. diet, especially information covering a larger geographic area in the United States is desirable. Also, few data are available regarding nickel levels at contaminated or hazardous waste sites (Bradley and Morris 1986; Duke 1980b; Taylor and Crowder 1983). This information is necessary for exposure assessment analysis at these sites. Since nickel is found in all soil, studies should focus on waste sites where nickel levels are substantially above those found in ordinary soil.

Exposure Levels in Humans. The nickel levels in body fluids, tissue, hair, nails, and breast milk are available (DiPietro et al. 1989; Hopfer et al. 1989; IARC 1990; Iyengar 1989; Takagi et al. 1986, 1988). Serum and urine levels in some exposed workers have also been published (Angerer and Lehnert 1990; Barceloux 1999; Bencko et al. 1986; Bernacki et al. 1978; Elias et al. 1989; Ghezzi et al. 1989; Hassler et al. 1983; Morgan and Rouge 1984; Oliveira et al. 2000; Torjussen and Andersen 1979). These data do not refer to populations living around the hazardous waste sites that contain elevated levels of nickel. Additional studies that examine nickel levels or make use of biomarker end points, such as changes in gene expression as measured with gene arrays, in body fluids and tissues from persons living near hazardous waste sites that contain elevated levels of nickel or have occupational exposures to nickel, would be useful.

6. POTENTIAL FOR HUMAN EXPOSURE

Exposure of Children. This information is necessary for assessing the need to conduct health studies on children. The nickel levels in urine are available (Baranowska-Dutkiewicz et al. 1992), but information on levels in other body fluids, tissue, hair, and nails is not available. These data do not refer to populations living around the hazardous waste sites that contain elevated levels of nickel. Additional studies that examine nickel levels in body fluids and tissues from children living near hazardous waste sites that contain elevated levels of nickel would be useful. Child health data needs relating to susceptibility are discussed in 3.12.2 Identification of Data Needs: Children's Susceptibility.

Exposure Registries. Although there is no U.S. exposure registry for nickel, a Finnish exposure registry for occupational carcinogens exists, and this registry contains information on nickel and inorganic nickel compounds (Grandjean 1984). This substance is not currently one of the compounds for which a subregistry has been established in the National Exposure Registry. The substance will be considered in the future when chemical selection is made for subregistries to be established. The information that is amassed in the National Exposure Registry facilitates the epidemiological research needed to assess adverse health outcomes that may be related to exposure to this substance.

6.8.2 Ongoing Studies

A number of ongoing studies concerning the fate/transport of nickel and human exposures to nickel were identified in the FEDRIP (2003) database. These studies are summarized in Table 6-7.

6. POTENTIAL FOR HUMAN EXPOSURE

Table 6-7. Ongoing Studies on Environmental Fate and the Potential for Human Exposure to Nickel^a

Investigator	Affiliation	Research description	Sponsor
Salt, DE	Purdue University	Identification of genes involved in nickel and zinc hyperaccumulation in plants	Hatch
Kpomblekou-Ademawou, K; Ankumah, RO	Tuskegee University	Determine total arsenic, chromium, copper, manganese, nickel, selenium, and zinc concentrations and the distribution of the chemical forms in soils under long-term broiler litter treatments	USDA
Chaney, RL	Beltsville ARC, Beltsville, Maryland	Characterize trace element adsorbents in municipal, industrial, and agricultural byproduct amended soils, which limit plant uptake and bioavailability of trace elements	USDA
Vincent, JH	University of Michigan	Develop a smaller and lighter sampling instrument to assess the occupational exposure of people to aerosol fractions most relevant to ill-health	NIH
Sparks, DL; Scheidegger, AM; Lamble, GM	University of Delaware	Determine the effects of residence time on the mechanisms of nickel sorption/release on soils and soil components and using this information to develop predictions about long-term fate of nickel in soils	NRI
Fiedler, NL	University of Medicine/Dentistry New Jersey	Develop a smaller and lighter sampling instrument to assess the occupational exposure of people to aerosol fractions most relevant to ill-health	NIH
Sweeney, JR	Clemson University	Determine normal concentrations in key tissues and normal whole-body burdens of selected heavy metals in wildlife inhabiting forested landscapes in the lower Atlantic Coastal Plain and effect of barker boiler ash land applications on the wildlife inhabitants	DOI, Bureau of Mines
Sparks, DL; Ford, RG	University of Delaware	Examine nickel and zinc sorption-desorption kinetic behavior on model and natural soil components, characterize structure of the sorption complex and investigate effect of competition of soil components with metal-Al precipitates	USDA
Tu, S	ERRC, Wyndmoor, Pennsylvania	Determine the kinetics and mechanism of heavy metal retention/release by soil mineral colloids as affected by inorganic anions and use information to predict long-term fate of metal in soil	USDA
Odom, JW	Auburn University	Develop analytical techniques for determining total and extractable heavy metals in Alabama soils and plant materials and assess the normal occurrence of metals in select soil profiles	Hatch

6. POTENTIAL FOR HUMAN EXPOSURE

Table 6-7. Ongoing Studies on Environmental Fate and the Potential for Human Exposure to Nickel^a

Investigator	Affiliation	Research description	Sponsor
McBride, MB	Cornell University	Develop methods to measure chemical lability of heavy metals in soils and soil materials, comparing labilities to solubility and plant availability and determine the forms that metals take in mineral soils over long terms	USDA
Helmke, PA; Bleam, WF	University of Wisconsin	Investigate the solubility behavior of major and trace element cations in an international suite of soils to determine whether adsorption-desorption or solubility phenomena controls the speciation and concentration of the dissolved trace elements	USDA
Fendorf, SE	University of Idaho	Ascertain the stability and redox reactivity of heavy retained on soil minerals	USDA
Ramachandran, G	University of Minnesota, Twin Cities	Develop an improved exposure and dose assessment method for epidemiologic research on occupational cancer that accounts for the uncertainties in exposure reconstruction due to sparse data, relevant dose, and exposures to multiple chemicals	NIH
Ross, DS	University of Vermont	Characterize the reactive sites on soil manganese oxides, determine differences between soil oxides and synthetic oxides, and elucidate mechanisms of surface oxidation reactions.	USDA
Kinraide, TB	ARS, Beaver, West Virginia	Elucidate physiological features of plants that determine heavy metal accumulation, binding characteristics of root plasma membranes, and correlate with genotypic differences in heavy metal accumulation	USDA
Hamilton, JW	Dartmouth College	Determine the impact of toxic metals found at Superfund sites, at other waste sites, and in the environment on adverse effects on human health and on the environment	NIH
Baligar, VC; Clark, RB; Zelazny, LC; Persaud, N; Ritchey, KD; Martens, DC	Virginia Polytechnic Institute	Evaluate mineralogy and chemistry of trace elements and sulfate in soil treated with coal-fired power plant by-products (CCB) and determine the co-utilization of CCB with organic amendments on changes in physical and chemical properties of soils	USDA
Volk, VV; Roseberg, RJ; Baham, J	Oregon State University	Assess potential of plants to remove trace metals from soils, identify plant nutrient requirements and determine impact of trace metals on plant health	Hatch
Bleam, WF; Helmke, PA	University of Wisconsin at Madison	Improve understanding of how humic substances in soil bind trace metals by elucidating specific binding sites and their affinities for trace metals	USDA

6. POTENTIAL FOR HUMAN EXPOSURE

Table 6-7. Ongoing Studies on Environmental Fate and the Potential for Human Exposure to Nickel^a

Investigator	Affiliation	Research description	Sponsor
Thompson, ML; Horton, R; Tabatabai, MA	Iowa State University	Identify and quantify the fundamental processes that determine the fate and transport of metals and pesticides once they are applied to the soil or where they occur in contaminated soils	USDA

^a FEDRIP 2003

ARC = Agricultural Research Center; ARS = Agricultural Research Service; DOI = Department of the Interior; ERRC = Eastern Regional Research Center; NIEHS = National Institutes of Environmental Health and Sciences; NIH = National Institutes of Health; NRI = National Research Institute; USDA = U.S. Department of Agriculture

